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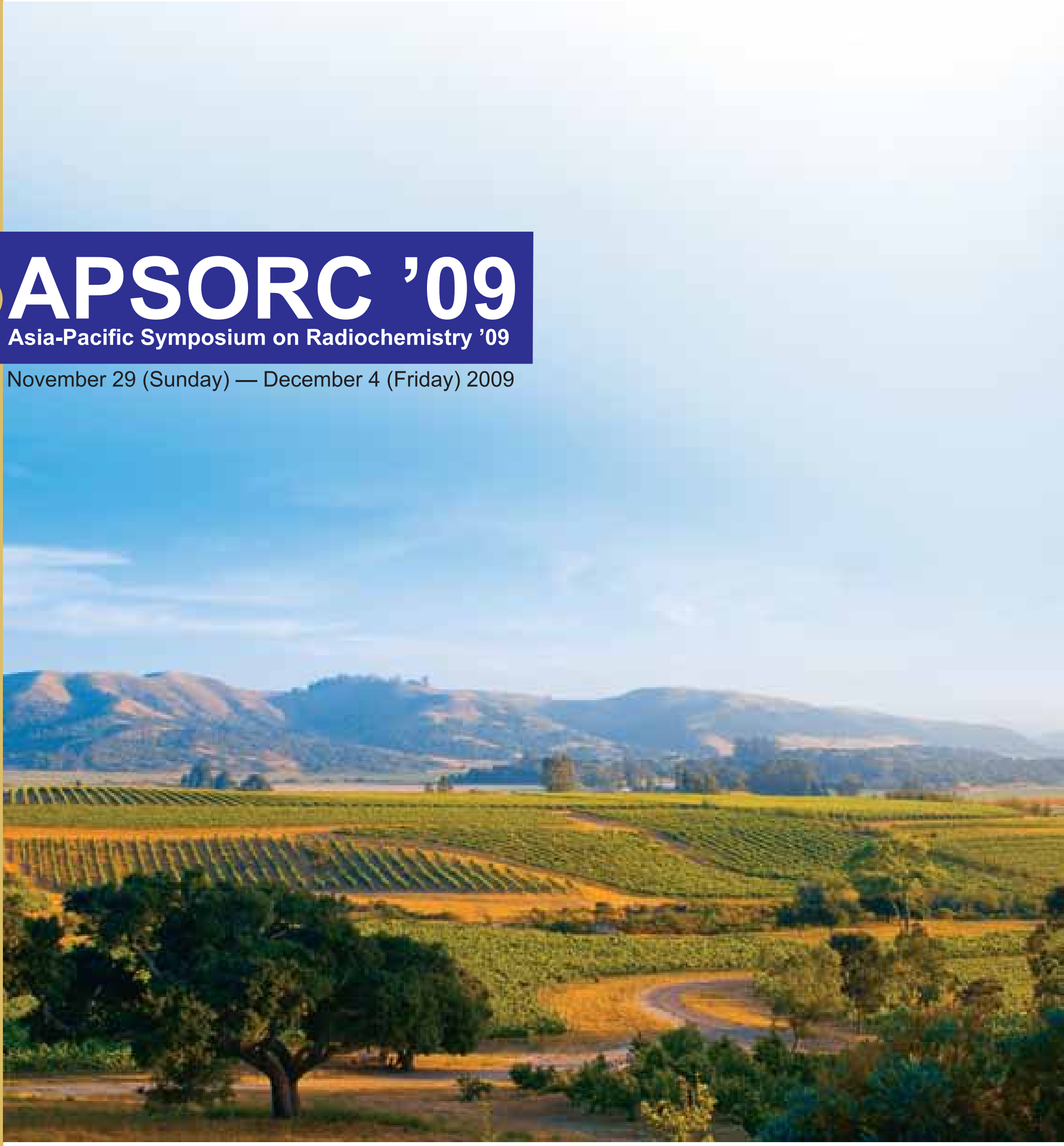
APSORC '09

Asia-Pacific Symposium on Radiochemistry '09

November 29 (Sunday) — December 4 (Friday) 2009



Abstracts

4th Asia-Pacific Symposium on Radiochemistry '09

November 29 – December 4, 2009
Napa Valley, California, U.S.A.

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The University of California Berkeley 1868

Washington State University
Lawrence Livermore National Laboratory
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Under the auspices of the APSORC International Committee (APSORC-IC), the Symposium is co-organized by:

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About the Symposium

The fourth international conference in the series of **A**sia-**P**acific **S**ymposium **o**n **R**adio**c**hemistry (APSORC-09) is held in Napa, California, U.S.A., from November 29 - December 4, 2009.

The first APSORC was held in Kumamoto, Japan (1997), the second in Fukuoka, Japan (2001), and the third in Beijing, China (2005). The conference provides an international forum for presentation and discussion of current and emerging sciences in all fields of radiochemistry and nuclear chemistry, and their applications to various fields. It aims to promote academic activities in nuclear, radiochemical and related sciences. Scientists, engineers and students from universities, institutes, laboratories and industries throughout the world are encouraged to participate and make contributions.

Conference papers will be peer-reviewed, and when accepted, will be published in *Radiochimica Acta*.

Scope

In addition to the discussions of the most recent experimental data and theoretical principles in all areas related to nuclear and radiochemistry, the Symposium will also focus on the future frontiers of research in the field. The scientific program consists of a series of invited plenary and topical lectures followed by presentations of invited and contributed papers in oral and poster sessions. The scientific program of the symposium has been developed by the session organizers of the individual subject areas.

Subject Areas -- APSORC covers the following topics related to Nuclear and Radiochemistry:

1. Education and future staffing needs in Nuclear and Radiochemistry at a national and global level. (Organizers: Chai Zhifang, China; J. Gutteridge, USA; F. Kinard, USA)
2. Nuclear forensics. (Organizers: K. Carney, USA; S. Clark, USA; S. LaMont, USA; Y. Miyamoto, Japan)
3. Radiation detection: Radiation dosimetry and metrology. (Organizers: H. Yasuda, Japan)
4. Nuclear energy chemistry, the Global Nuclear Energy Partnership (GNEP), and Global Warming: Fuel reprocessing and new separation process; nuclear waste management and disposal; nuclide migration and performance assessment of geologic (high-level) nuclear repositories. (Organizers: H. Funasaka, Japan; S. Kalmykov, Russia; Chunli Liu, China; T. Todd, USA; N. Wall, USA)
5. Nuclear reactions, nuclear decay/structure/cross sections, nuclear fission, heavy and super heavy elements science. (Organizers: W. Loveland, USA; Y. Nagame, Japan; Guo-Qing Xiao, China)
6. Radioactive isotope beams. (Organizers: W. Loveland, USA; Y. Nagame, Japan; Guo-Qing Xiao, China)
7. Actinide science. (Organizers: Jun Li, China; T. Kimura, Japan; Z. Wang, USA; R. Wilson, USA; Z. Yoshida, Japan)
8. Environmental radiochemistry and radioecology. (Organizers: K. Inn, USA; N. Momoshima, Japan; B. Salbu, Norway)
9. Nuclear analytical techniques: Neutrons; Ions; X-ray; Synchrotron radiation, etc. (Organizers: Hee-Dong Choi, Korea; R. Lindstrom, USA; T. Nakanishi, Japan)
10. Radiopharmaceutical chemistry, including Tc chemistry, nuclear imaging, and radioisotope production. (Organizer: H. VanBrocklin, USA)
11. Applications of nuclear & radiochemical techniques in Life Science; Nano Science; Environmental Science; Geo- and Cosmo sciences, Archaeology; etc. (Organizers: G. Geipel, Germany; C. Walther, Germany)
12. Nuclear probes for new materials: Mössbauer; perturbed angular correlations; positron annihilation, etc. (Organizer: K. Nomura, Japan)

Program

Sunday, November 29, 2009

1500-2000	Registration
1700-1730	Opening Ceremony & Welcoming Addresses
1730-1800	Darleane Hoffman – *UC Berkeley and Lawrence Berkeley National Laboratory* – "History of the Periodic Table"
1800-1830	James Conca – *New Mexico State University* – "How Much Energy do we Need for a Just and Sustainable Future?"
1830-1930	Reception

Technical Program

Monday, November 30, 2009

Session 1 – Plenary (invited) Room A

Chairs: D.C. Hoffman, N. Nakahara

0830-0900	1-PS4	Terry Todd	Actinide Separations in the U.S. Advanced Fuel Cycle Initiative	Subject 4
0900-0930	1-PS7	Klaus Mayer	Investigative Radiochemistry – A Key Element in Nuclear Forensics	Subject 7
0930-1000	1-PS8	Brit Salbu	The Relevance of Radioactive Particles in the Environment	Subject 8

Session 2 – Subject 8: Environmental Radiochemistry and Radioecology Room A

Chairs: N. Momoshima, A. Kersting

1015-1045	2-TS8-1	Peter Stegnar (invited)	Legacy of Uranium Extraction and Environmental Security in the Central Asian Republics of Kazakhstan, Kyrgyzstan, Tajikistan and Uzebekistan
1045-1100	2-S8-2	Wangsuo Wu	Sorption of Eu(III) on Attapulgite, ZSM-5 and MWCNTS: Studied by Batch, XPS and EXAFS Techniques
1100-1115	2-S8-3	Henry Moll	A Comparative Complexation Study on Np(V) Interactions With Bacterial Cell Wall Compartments and Bioligands Secreted by Microbes
1115-1130	2-S8-4	Nick Evans	Aspects of the Complexation of Tc(IV) with Organic Ligands in UK Radioactive Waste Disposal
1130-1145	2-S8-5	Seiya Nagao	Radiocarbon of Aquatic Humic and Fulvic Acids in the Chikugo River Waters
1145-1200	2-S8-6	Sergei Tolmachev	The U.S. Transuramium and Uranium Registries: Forty Years' Experience and New Directions in the Analysis of Actinides in Human Tissues

Session 3 – Subject 4: Nuclear Energy Chemistry, the Global Nuclear Energy Partnership (GNEP), and Global Warming: Fuel Reprocessing and New Separation Process; Nuclear Waste Management and Disposal; Nuclide Migration and Performance Assessment of Geologic (High-Level) Nuclear Repositories Room B

Chairs: H. Funasaka, S. M. Kalmykov

1015-1045	3-TS4-1	Chunli Liu (invited)	Current Status of High-Level Radioactive Waste Disposal in China
1045-1100	3-S4-2	Stepan Kalmykov	Actinide Interaction With Groundwater Colloids: Sorption at Femto- To Micromolar Concentration Range and Surface Complexation Modelling
1100-1115	3-T4-3	Nathalie Wall	The Dynamics of Hexavalent Uranium Mineral Dissolution and Sorption
1115-1130	3-S4-4	Takeshi Ogata	Extraction Properties of Podand-type Nitrogen Donor Ligands Toward Oxoanions
1130-1145	3-S4-5	David Wickendon	Treatment of Radioactive Contaminated Oily Wastes Using Adsorption Coupled With Electrochemical Regeneration
1145-1200	3-S4-6	Yuji Sasaki	Extraction of Technetium(VII) and Rhenium(VII) by the New Reagent, 2-(lmino)bis(N,N-dialkylacetamide) (IDAA)

Session 4 – Plenary (working lunch), Subject 1: Education and Future Staffing Needs in Nuclear and Radiochemistry at a National and Global Level Room C

Chair: F. Kinard

1200-1330	4-PS1	Wangsuo Wu	Radiochemical Education and Training in China

Session 5 – Subject 8: Environmental Radiochemistry and Radioecology Room A

Chairs: B. Salbu, P. Strand

1330-1400	5-TS8-1	Noriyuki Momoshima (invited)	Evaluation for Po-210 Intake through Fish and Shellfish Consumption by Japanese
1400-1415	5-S8-2	Yung-Jin Hu	Reaction of Plutonium(VI) with Manganese-Substituted Goethite
1415-1430	5-S8-3	Tomoko Ohta	Observation of 228Ra/226Ra Activity Ratio, and Concentrations of 226Ra and 228Ra of Surface Seawaters in the Pacific Side of Japan
1430-1445	5-S8-4	Aya Sakaguchi	First Results on 236U Level in Soils from Global Fallout – Application for Hiroshima Black-Rain Issue
1445-1500	5-S8-5	Myung Ho Lee	Determination of Plutonium, Uranium, Strontium and Americium/Curium Isotopes in Environmental Samples with Anion Exchange, UTEVA, Sr and DGA Resin
1500-1515	5-S8-6	Lindis Skipperud	Po-210 in Water and Fish from Central Asia Uranium Mining and Tailing Sites
1515-1530	5-S8-7	Dominic Peterson	Rapid Separation and Extraction of Radioactive Analytes onto Filters and Membranes
1530-1545		**Break**	
1545-1600	5-S8-8	Per Strand	Radioactivity in the Arctic Environment
1600-1615	5-S8-9	Jack Bennett	Increasing Radioanalytical Capacity – Preparing Your Lab
1615-1630	5-S8-10	Ken Fujimoto	Isolation, Cloning and Characterization of Silver-110m Binding Protein (Hemocyanin-TPb) from Liver of Squid
1630-1645	5-S8-11	Martin Johnson	Automated Radionuclide Separations System for Field Laboratory and/or Fixed Laboratory Use
1645-1700	5-S8-12	Annie Kersting	Structure of Plutonium Colloids when Associated with Different Minerals
1700-1715	5-S8-13	Yutaka Miyamoto	Sequential Anion Exchange Separation of Trace Uranium, Thorium, Lead and Lanthanides in Environmental Samples
1715-1730	5-S8-14	Terry Hamilton	Accelerator Mass Spectrometric Measurements of Plutonium Isotopes in Soil Samples Collected from Enewetak Atoll in the Northern Marshall Islands

Session 6 – Subject 4: Nuclear Energy Chemistry, the Global Nuclear Energy Partnership (GNEP), and Global Warming: Fuel Reprocessing and New Separation Process; Nuclear Waste Management and Disposal; Nuclide Migration and Performance Assessment of Geologic (High-Level) Nuclear Repositories Room B

Chairs: C.L. Liu, N. Wall

1330-1400	6-TS4-1	Hajimu Yamana (invited)	Perspective on Japanese Fuel Cycle and Expectation to Technical Advancements
1400-1415	6-S4-2	Hideyuki Funasaka	Current Status and Perspective on Fast Reactor Fuel Cycle Technology Development Project in Japan
1415-1430	6-S4-3	Ken Nash	Approaches to Managing Minor Actinides in Advanced Nuclear Fuel Cycles
1430-1445	6-S4-4	Kenji Takeshita	Extraction Separation of Trivalent Minor Actinides from Lanthanides with Hexadentate Nitrogen-Donor Ligands, TPEN and Its Derivatives
1445-1500	6-S4-5	Jan John	Am/Eu Chromatographic Separation with New Solid Extractants Based on C5-BTBP
1500-1515	6-S4-6	Hiromu Kurosaki	Chromatographic Separation of Am and Cm
1515-1530	6-S4-7	Joseph Lapka	The Extraction of Actinides with Diamides of Dipicolinic Acid
1530-1545		**Break**	

Session 6 – Subject 7: Actinide Science Room B

Chairs: J. Li, R. Wilson

1545-1615	6-TS7-8	David Morris (invited)	Organometallic Actinide Chemistry: New Platforms for Manipulation and Eluciation of Molecular and Electronic Structure
1615-1630	6-S7-9	Yoshinori Haga	Novel Magnetism and Superconductivity in Actinide-Based Intermetallic Compounds
1630-1645	6-S7-10	Zheming Wang	An Optical Spectroscopy Investigation of Environmental Effects on Uranium Oxyfluoride Particles
1645-1700	6-S7-11	Krishnan Balasubramanian	Recent Computational Studies of Actinide Complexes and Their Reactions
1700-1715	6-S7-12	Travis Bray	Electrospray and Gas-Phase Behavior of Cerium Phosphomolybdates: A Prelude to Plutonium Chemistry
1715-1730	6-S7-13	Takaumi Kimura	Time-Resolved Laser Fluorescence Microscopy (TRLFM) for Adsorption Study of Luminescent f-Element on a Heterogeneous Surface

Poster Session 1, 1730-2030

Subject Areas: 2 - Nuclear Forensics; 4 - Nuclear Energy Chemistry, the Global Nuclear Energy Partnership (GNEP), and Global Warming: Fuel Reprocessing and New Separation Process; Nuclear Waste Management and Disposal; Nuclide Migration and Performance Assessment of Geologic (High-Level) Nuclear Repositories; 7 - Actinide Science; 8 - Environmental Radiochemistry and Radioecology

Tuesday, December 1, 2009

Session 7 – Plenary (invited) Room A

Chairs: T.A. Todd, Z. Yoshida

0830-0900	7-PS5	Matthias Schädel	Superheavy Element Research at TASCA	Subject 5
0900-0930	7-PS6	Isao Tanihata	Looking for the Effect of Tensor Forces in Nuclei	Subject 6
0930-1000	7-PS11	Heinz Gäggeler	Microanalytical 14C AMS Measurements on Carbonaceous Particles	Subject 11

Session 8 – Subject 7: Actinide Science Room A

T. Kimura, Z. Wang

1015-1045	8-TS7-1	Christopher Cahill (invited)	Hybrid Materials from the An Elements: Synthesis, Structure and Spectroscopy
1045-1100	8-S7-2	Richard Wilson	The Surface Chemistry of Colloidal Plutonium
1100-1115	8-S7-3	Jun Li	Relativistic DFT Investigations of NMR Properties of Actinide Compounds
1115-1130	8-S7-4	Yoko Kokubu	Plutonium of Nagasaki Atomic Bomb Deposited Around Nagasaki, Japan
1130-1145	8-S7-5	Yoshio Takahashi	High-Sensitive Measurement of U LIII-Edge X-Ray Absorption Near-Edge Structure Using Bent Crystal Analyzer for the Determination of the Oxidation States of Uranium in Crustal Materials
1145-1200	8-S7-6	Aurora Clark	Trends in Ln(III) Sorption to Defect Ridden Quartz: Insights from a Multiscale Computational Approach

Session 9 – Subject 5: Nuclear Reactions, Nuclear Decay/Structure/Cross Sections, Nuclear Fission, Heavy and Super Heavy Elements Science Room B

Chairs: W. Loveland, M. Block

1015-1045	9-TS5-1	Hiromitsu Haba (invited)	Present Status and Perspectives of Super Heavy Element Chemistry at Riken
1045-1100	9-S5-2	Roger Henderson	Estimating Super Heavy Element Event Random Probabilities Using Monte Carlo Methods
1100-1130	9-S5-3	Kenneth Gregorich	Understanding (Super) Heavy Element Cross Sections
1130-1145	9-S5-4	Qin Zhi	Nuclear Chemistry of Actinides and Transactinides at IMP
1145-1200	9-S5-5	Atsushi Toyoshima	Electrochemistry of the Heaviest Elements at JAEA

Session 10 – Plenary (working lunch), Subject 1: Education and Future Staffing Needs in Nuclear and Radiochemistry at a National and Global Level

Room C

Chair: J. Gutteridge

1200-1330	10-PS1	Akihiko Yokoyama	Present Situation and Future Prospects on Nuclear and Radiochemistry Education in Japan

Session 11 – Subject 11: Applications of Nuclear & Radiochemical Techniques in Life Science; Nano Science; Environmental Science; Geo- and Cosmo Sciences, Archaeology; etc.

Room A

Chairs: G. Geipel, C. Walther

1330-1400	11-TS11-1	Zhiyong Zhang (invited)	Nuclear Analytical Techniques for Nanotoxicology Studies
1400-1415	11-S11-2	Joao Arruda-Neto	Probing Bio-Nanostructures (DNA) with Ionizing Radiation: Perspectives for Improving Cancer Radiotherapy
1415-1430	11-S11-3	Clemens Walther	The Role of Polymerization and (Pseudo) Colloid Formation for Understanding the Behavior of An Ions in Aqueous Solution
1430-1445	11-S11-4	Wolfgang Kretschmer	Application of Accelerator Mass Spectrometry to Archaeology, Geography and Environmental Science
1445-1500	11-S11-5	Hirotaka Oda	Radiocarbon Age of Miidera-Gire Attributed to Enchin and the Historical Age in which an Ancient Manuscript of Monzen Was Written
1500-1515	11-S11-6	Yuichi Kurihara	Radioactive Equilibria and Disequilibria of U-Series Nuclides in the Products from Izu Arc Volcanoes, Japan
1515-1530	11-S11-7	Toshiyuki Fujii	Nuclear Field Shift Effect in Isotope Fractionation of Palladium Using a Crown Ether
1530-1545		**Break**	
1545-1615	11-TS11-8	Peter Englert (invited)	Orbital Planetary Gamma Ray Spectroscopy: From Concept to Success
1615-1645	11-TS11-9	Gerhard Geipel (invited)	Interaction of Uranium(VI) Towards Glutathione – An Example to Study Different Functional Groups in One Molecule
1645-1700	11-S11-10	Katrin Viehweger	Glutathione – A Key Factor of Uranium Tolerance in Plant Cells
1700-1730	11-S11-11	Dorothea Schumann	Separation of 60Fe Samples from an Irradiated Beam Dump for Nuclear Astrophysics Experiments

Session 12 – Subject 5: Nuclear Reactions, Nuclear Decay/Structure/Cross Sections, Nuclear Fission, Heavy and Super Heavy Elements Science and Subject 6: Radioactive Isotope Beams Room B

Chair: Y. Nagame, M. Schädel

1330- 1400	12-TS6-1	Jens Dilling (invited)	Penning Trap Experiments on the Most Exotic Nuclei on Earth: Mass Measurements of Halo Nuclei at TITAN
1400- 1415	12-S5-2	Michael Block	First Direct Mass Measurements of 252-254No with SHIPTRAP
1415- 1430	12-S5-3	Rod Clark	Isomer Spectroscopy of the Heaviest Elements
1430- 1445	12-S5-4	Yuichiro Nagame	Chemical Investigation of Rf and Db at JAEA
1445- 1500	12-S5-5	Roger Henderson	Recent Updates in Heavy Element Production from LLNL
1500- 1515	12-S5-6	Rugard Dressler	The Challenge of Using a Physical Preseparator in Chemical Experiments with Super Heavy Elements: The Stopping Force Problem
1515- 1530	12-S5-7	Megan Bennett	Extraction Chromatographic Studies of Rf and Db Homologs
1530- 1545		**Break**	
1545- 1600	12-S5-8	Hiroyuki Koura	Decay Modes and a Limit of Existence of Nuclei in the Super Heavy Mass Region
1600- 1615	12-S5-9	Kougi Morimoto	Production and Decay Properties of 266Bh and 262Dd by Using the 248Cm(23Na,5n) Reaction
1615- 1630	12-S5-10	Irena Dragojevic	Systematic Studies of Nuclear Fusion Reactions at Low Excitation Energies with 208Pb Targets and Pairs of Projectiles Differing by Two Neutrons
1630- 1645	12-S5-11	P. K. Pujari	Evaporation Residue Cross Sections in 28Si + 176Yb Reaction
1645- 1700	12-S5-12	Bethany Goldblum	Indirect Determination of Neutron Capture Cross Sections Using the Surrogate Ratio Method
1700- 1715	12-S5-13	Tsutomu Ohtsuki	Half-Life Measurement of Be-7 in Buckyballs and Host Metals
1715- 1730	12-S6-14	Walter Loveland	The Fusion of 9Li with 20Pb

Poster Session 2, 1730-2030

Subject Areas: 3 - Radiation Detection: Radiation Dosimetry and Metrology; 5 - Nuclear Reactions, Nuclear Decay/Structure/Cross Sections, Nuclear Fission, Heavy and Super Heavy Elements Science; 9 - Nuclear Analytical Techniques: Neutrons; Ions; X-Ray; Synchrotron Radiation, etc.; 10 - Radiopharmaceutical Chemistry, Including Tc Chemistry, Nuclear Imaging, and Radioisotope Production; 11 - Applications of Nuclear & Radiochemical Techniques In Life Science, Nano Science, Environmental Science, Geo- and Cosmo Sciences, Archaeology; etc.; 12 - Nuclear Probes for New Materials: Mössbauer, Perturbed Angular Correlations, Positron Annihilation, etc.

Wednesday, December 2, 2009

Session 13 – Plenary (invited) Room A

Chair: H-D. Choi, T. Kishikawa

0830- 0900	13-PS12	Amar Nath	The Role of Emission Mössbauer Spectroscopy in the Study of Sophisticated Materials	Subject 12
0900- 0930	13-PS10	John Valliant	New Strategies for the Discovery, Production and Translation of Novel Molecular Imaging Probes	Subject 10

Subject 10: Radiopharmaceutical Chemistry, Including Tc Chemistry, Nuclear Imaging, and Radioisotope Production Room A

Chair: H. VanBrocklin, J. Valliant

0930-0945	13-S10-1	Suresh Srivastava	Production and Use of Tin-117m for Application to Therapy of Cancer in Bone
0945-1000	13-S10-2	Jerry Nolen	Energy-Efficient, Accelerator-Driven Production of 99Mo

Session 14 – Subject 12: Nuclear Probes for New Materials: Mössbauer; Perturbed Angular Correlations; Positron Annihilation, etc. Room B

Chair: G. Klingelhöfer, K. Nomura

1015-1045	14-TS12-1	Anita Hill (invited)	Positron Studies of Polymer Thin Films
1045-1100	14-S12-2	Yoshinori Kobayashi	Study of Polymers by Positron Annihilation Spectroscopy
1100-1115	14-S12-3	Franz Renz	Physical and Chemical Induced Spin Crossover
1115-1130	14-S12-4	Kiyoshi Nomura	Characterization of 57Fe implanted SnO2 films by Mossbauer spectroscopy and Nuclear Inelastic Scattering
1130-1145	14-S12-5	Goestar Klingelhöfer	57Fe Mössbauer Spectroscopy with Mimos II at the Surface of Mars
1145-1200	14-S12-6	Takashi Nagatomo	Improvement of Signal-To-Noise Ratios in 57Mn Impantation Mössbauer Spectroscopy

Session 15 – Subject 10: Radiopharmaceutical Chemistry, Including Tc Chemistry, Nuclear Imaging, and Radioisotope Production Room A

Chair: H. VanBrocklin, J. Valliant

1015-1045	15-TS10-1	Tom Ruth (invited)	Production of Mo-99 and Tc-99M Via Alternative Routes
1045-1100	15-S10-2	Yuchi Hatsukawa	Isotope Production for Medical Usage Using Fast Neutron Reactions
1100-1115	15-S10-3	Van So Le	Theoretical Assessment of Specific Radioactivity: The Effect of Target Burn-Up, Isotope Dilution and Target Purity and the Application for Lu-177 Production
1115-1130	15-S10-4	Paul Forster	Technetium Bromides: Fundamental Studies and Advances Towards the Syntheses of Low Valent Technetium Complexes
1130-1145	15-S10-5	Sandrine Huclier-Markai	Evaluation of Scandium-Polyaminopolycarboxylic Complexes as a New Generation of PET Agent and Radiopharmaceutical
1145-1200	15-S10-6	Henry VanBrocklin	Efficient Approaches to Labeling Radiopharmaceuticals with Fluorine-18

1200-1400	No-host lunch
1400-1730	Excursion to wineries
1730-1800	Bus from hotel to dinner
1800-2200	Conference Dinner Speaker: Siegfried Hecker

Thursday, December 3, 2009

Session 16 – Plenary (invited) Room A

Chair: A. Chatt, Y. Maeda

0830-0900	16-PS9	Tomoko Nakanishi	Application of Radioisotope Measurement for Plant Study – From Activation Analysis to Radioisotope Imaging	Subject 9
0900-0930	16-PS2	Siegfried Hecker	Why Nuclear Forensics?	Subject 2
0930-1000	16-PS3	Seiichi Shibata	Measurement of Nickel-63 for Reassessment of Neutron Dosimetry for the Hiroshima Atomic Bomb	Subject 3

Session 17 – Subject 2: Nuclear Forensics Room A

Chair: K. Carney, S.B. Clark

1015-1045	17-TS2-1	Jon Schwantes (invited)	Nuclear Archeology in a Bottle: Evidence of Pre-Trinity U.S. Weapons Activities from a Waste Burial Site
1045-1100	17-S2-2	Kenichiro Yasuda	Instrumental Development for Measurement of Elemental Distribution on Swipe Samples for Safeguards
1100-1115	17-S2-3	Russell Gritzo	Development of a High Purity Germanium Detector Clover System at Los Alamos National Laboratory
1115-1130	17-S2-4	Christopher McGrath	Further Development of a Portable Liquid Scintillation System with Alpha/Beta Discrimination
1130-1145	17-S2-5	Michael Savina	Sequestration and Analysis Methods for Lanthanides and Actinides Using Resonance Ionization Mass Spectrometry
1145-1200	17-S2-6	Ruth Kips	Measuring Flourine in Uranium Oxyflouride Particles Using Secondary Ion Mass Spectrometry for Nuclear Forensics

Session 18 – Subject 9: Nuclear Analytical Techniques: Neutrons; Ions; X-Ray; Synchrotron Radiation, etc. Room B

Chair: R. Lindstrom, T.M. Nakanishi

1015-1045	18-TS9-1	Richard Firestone (invited)	Comparison of IUPAC k0 Values and Neutron Cross Sections to Determine a Self Consistent Set of Data for Neutron Activation Analysis
1045-1100	18-S9-2	Vladimir Kolotov	Development of Nuclear Image Methods of Analysis Based on Gamma Activation
1100-1115	18-S9-3	Zhifang Chai	Metallomics Study – A Nuclear Approach
1115-1130	18-S9-4	Yuchi Hatsukawa	Isotope Production for Medical Usage Using Fast Neutron Reactions
1130-1145	18-S9-5	Masumi Oshima	Application of Triple Gamma Coincidence in Prompt Gamma-Ray Analysis and Neutron Activation Analysis
1145-1200	18-S9-6	Daniel Cummings	Application of Gas Pressurized Extraction Chromatography (GPEC) to the Analytical Laboratory

Session 19 – Plenary (working lunch), Subject 1: Education and Future Staffing Needs in Nuclear and Radiochemistry at a National and Global Level Room C

Chair: Z. Chai

1200-1330	19-PS-1	Heino Nitsche	Nuclear and Radiochemistry Education in the USA: Crisis or Turning Point?

Session 20 – Subject 2: Nuclear Forensics Room A

Chairs: S. LaMont, Y. Miyamoto

1330-1400	20-TS2-1	Ian Hutcheon (invited)	Nuclear Forensics: An Emerging and Still Imperfect Science
1400-1415	20-S2-2	Jay Grate	Acceleration and Automation of Actinide Analysis Methods
1415-1430	20-S2-3	Amanda Klingensmith	Surface Analysis of Electrodeposited Actinide Sources for Alpha Spectroscopy
1430-1445	20-S2-4	Ralf Sudowe	Development of Rapid Separation Techniques for Nuclear Forensics
1445-1500	20-S2-5	Douglas Duckworth	Validation of Electrochemically Modulated Separations On-Line with MC-ICP-MS as a Means of Rapid Low-Level U-Pu Isotopic Analysis
1500-1515	20-S2-6	Paul Schumacher	Optimization of Nd(III) Pre-Concentration on a Rotating Disk Mercury Film Electrode in Aqueous Solution
1515-1530		**Break**	
1530-1545	20-S2-7	David Podlesak	Application of Guide to the Expression of Uncertainty in Measurement (GUM) to U and Pu Isotope Ratios Measurements by Thermal Ionization Mass Spectrometry (TIMS)
1545-1600	20-S2-8	Ken Czerwinski	Imaging and Microscopy Techniques in the Examination of a Plutonium Hot Particle: Application to Nuclear Forensics
1600-1615	20-S2-9	Donna Beals	Analysis of Spent Research Reactor Fuel to Support Nuclear Forensic Programs
1615-1630	20-S2-10	David Gerlach	Isotope Ratio Techniques to Determine Energy Production in Reactors
1630-1645	20-S2-11	Dominic Peterson	Trace Elemental Analysis Capabilities for the Characterization of Radioactive and Stable Isotopes from Aerosol Particles on Marple Substrates
1645-1700	20-S2-12	Nicholas Lloyd	The Forensic Analyses of Uranium Oxide Particles from the Colonie Environmental Case-Study
1700-1715	20-S2-13	Zsolt Varga	Recent Development Work on Nuclear Forensic Signatures in Natural Uranium
1715-1730	20-S2-14	Michael Kristo	Nuclear Forensic Signatures in Commercial Nuclear Fuels

Session 21 – Subject 9: Nuclear Analytical Techniques: Neutrons; Ions; X-Ray; Synchrotron Radiation, etc. Room B

Chairs: Y. Hatsukawa, V. Kolotov

1330-1400	21-TS9-1	Amares Chatt (invited)	Preconcentration of Copper by Cloud Point Extraction with 1-(2-Pyridylazo)-2-Naphthol and Determination by Neutron Activation
1400-1415	21-S9-2	Hee Dong Choi	New Features of HYPERGRAM for HPGe Gamma-Ray Spectrum Analysis
1415-1430	21-S9-3	Richard Lindstrom	Uncertainty of Gamma-Ray Peak Integration
1430-1445	21-S9-4	Mohammad Islam	Non-Destructive Analysis of Bulky Meteorites by Neutron-Induced Prompt Gamma-Ray Analysis
1445-1500	21-S9-5	Jong-Myoung Lim	Comparative Study for Airborne Toxic Metal Determination by INAA and CCT-ICP-MS
1500-1515	21-S9-6	P. K. Pujari	Large Sample NAA by k0-Based Internal Mono Standard Method Using In-Situ Detection Efficiency
1515-1530		**Break**	

Session 21 – Subject 3: Radiation Detection: Radiation Dosimetry and Metrology Room B
Chairs: S. Shibata, H. Yasuda

1530-1600	21-TS3-7	Alexander Plionis (invited)	Improved Committed Effective Dose Estimates for Uranium Foundry Processes Using Marple Cascade Impactors
1600-1615	21-S3-8	Hiroki Fujita	Using Soils for Accident Dosimetry: A Preliminary Study Using Optically Stimulated Luminescence from Quartz
1615-1630	21-S3-9	Thomas Semkow	Origins of Seasonal Oscillations in Radioactive Exponential Decay
1630-1645	21-S3-10	Hiroko Ohuchi	Tritium Measurement by Using a Photo-Stimulable Phosphor BaFBr(I):Eu2+ Plate
1645-1700	21-S3-11	Jae Woo Park	Gamma Ray Dosimetry in a 60Co Irradiation Chamber with a Small Piece of CWO Scintillator and Gap Photodiode
1700-1715	21-S3-12	Martin Andersson	Application for Simple and Quick Calculation of Aviation Route Doses

Friday, December 4, 2009

Session 22 - Education and Future Staffing Needs in Nuclear and Radiochemistry at a National and Global Level Room A
Chairs: M. Ebihara, F. Kinard

0830-0844	22-S1-1	Alice Mignerey	Expanding the Pipeline – Nuclear Science Education for the 21st Century
0844-0858	22-S1-2	Sue Clark	Academic Radiochemistry Program in a Chemistry Department: The Experience at Washington State University
0858-0912	22-S1-3	Silvia Jurisson	Radiochemistry Training at the University of Missouri: A Program with a Long Half-Life
0912-0926	22-S1-4	Ralf Sudowe	Radiochemistry Education at the University of Nevada Las Vegas
0926-0940	22-S1-5	Brian Powell	A Multidisciplinary Teaching and Research Approach: Environmental Radiochemistry at Clemson University
0940-0954	22-S1-6	Tom Lönnroth	On the Need of Education in Nuclear Energy Systems: Problems and Challenges for a Small University
0954-1008	22-S1-7	P. N. Mehrotra	Nuclear Knowledge Management in India: Present Status and Future Projection
1008-1022	22-S1-8	Annie Kersting	Nuclear Forensics Summer Student Program at Lawrence Livermore National Laboratory
1022-1036	22-S1-9	Frank Kinard	The American Chemical Society/Department of Energy Nuclear Summer School Program
1036-1050	22-S1-10	Craig Williamson	New Integrated Efforts in University Programs to Support Radiochemistry Workforce Development
1050-1105		**Break**	

1105-1145 Roundtable - Education and Future Staffing Needs in Nuclear and Radiochemistry at a National and Global Level

Moderators: F. Kinard and M. Lambregts

Panel: S. B. Clark (USA), M. Ebihara (Japan), S. Jurisson (USA), A. Mignerey (USA), C. Williamson (USA), W. Wu (P.R. China)

1145-1200 Closing Ceremony

APSORC ’09 Poster Sessions

Poster Session I – Monday, November 30, 2009 – 5:30 – 8:30 PM

Subject Area 2 – Nuclear Forensics

PO-1-2-1	Paul Ellison	Fundamental Low Energy Nuclear Science Research for Nuclear Forensics: Producing Americium-240
PO-1-2-2	Judah Friese	Chemical Consideration of Radionuclide Leakage From Underground Nuclear Tests
PO-1-2-3	Amy M. Gaffney	230Th-234U Model Ages of Some Uranium Standard Reference Materials
PO-1-2-4	Brett Isselhardt	Development of Resonance Ionization Mass Spectrometry for Measuring Uranium Isotope Ratios in Nuclear Materials
PO-1-2-5	Kim B. Knight	Application of Resonance Ionization Mass Spectrometry to Detection of Uranium in Natural Silicate Matrices
PO-1-2-6	Stephen LaMont	Recent Improvements to the Environmental Safeguards Analysis Program at Los Alamos
PO-1-2-7	Yutaka Miyamoto	QA/QC activities and estimation of uncertainty for ultra-trace analysis of uranium and plutonium in safeguards environmental samples
PO-1-2-8	Dominic S. Peterson	Physical properties of oxidized nuclear materials
PO-1-2-9	Martin Robel	Nuclear Forensic Inferences Using Iterative Multidimensional Statistics
PO-1-2-10	Ross W. Williams	Local and Global Fallout Preserved in Lake Sediment from the Sierra Nevada, California

Subject Area 4 - Nuclear engery chemistry, the Global Nuclear Energy Partnership (GNEP), and Global Warming: Fuel reprocessing and new separation process; nuclear waste management and disposal; nuclide migration and performance assessment of geologic (high-level) nuclear repositories

PO-1-4-1	Yoichi Arai	Study on Solvent Cleanup Using Activated Alumina for Purex Process
PO-1-4-2	Sang-Eun Bae	Alloy Formation of Actinides or Lanthanides during Electrochemical Deposition in LiCl-KCl Eutectic
PO-1-4-3	M. Alex Brown	Complexation of Pu(IV) with Acetohydroxamic Acid: Solvent Extraction with Di(20Ethylhexyl) Phosphoric Acid
PO-1-4-4	Zhifang Chai	Chromatographic Partitioning of Cesium from Simulated HLW Using a Macroporous Silica-Based Calix[4]arene Impregnated Supramolecular Recognition Composite
PO-1-4-5	Ken Czerwinski	Monitoring of Spent Nuclear Fuel Reprocessing Studies by UV-Visible Spectroscopy
PO-1-4-6	Jean-Phillippee Dancausse	Dissolution, an Essential Step for Analysis of Irradiated Fuels and Targets: Atalante Experiments and Studies
PO-1-4-7	Isabelle Dubois	Radionuclide Sorption on Granitic Material: Effect of the BET Surface Area and Particle Size
PO-1-4-8	Bernadette Ferencz	The Results of Fuel Leak Tests at Unit 4 of PAKS Nuclear Power Plant
PO-1-4-9	Manjusha Karve	Amberlite XAD-2 Impregnated Cyanex272: Sorption Desorption Studies of Th(IV)
PO-1-4-10	Rie Kurata	Kinetics study on migration processes of energetic deuterium implanted into boron films
PO-1-4-11	Chun-li Liu	The Speciation and Solubility of Americium in Beishan Groundwater
PO-1-4-12	Maria Lucanikova	Cobalt Bis(Dicarbollide) Ion Derivates Covalently Bonded with Diglycolydiamide for Lanthanide and Actinide Extraction
PO-1-4-13	Vijay Kumar Manchanda	Partitioning and Transmutation - International Scenario

PO-1-4-14	Vijay Kumar Manchanda	Selective recovery of cesium using hollow fibre supported liquid membrane containing calix[4]arene-bis-2,3-naphtho-crown-6
PO-1-4-15	Edward Mausolf	Application of Acetohydroxamic, Formohydroxamic, and Ascorbic Acid in Nuclear Reprocessing: Complexation with Technetium 99 and Implications to the UREX Process
PO-1-4-16	Adam Menyhart	The Results of Inhermeticity Measurements of Fuel Cells in Unit 4 of the PAKS Nuclear Power Plant
PO-1-4-17	Kenji Okuno	Role of energetic tritium chemistry on developing thermonuclear fusion reactors
PO-1-4-18	Yuri Ostrovsky	Improvement of Technology for Nitric Acid Extraction Affinage of Uranium
PO-1-4-19	Yuri Ostrovsky	Rehabilitation of Uranium Productions Technogenic Watertanks
PO-1-4-21	Frederic Poineau	Synthesis and Corrosion of Metallic Technetium in Acidic Media
PO-1-4-22	Ge Sang	Recombination of Hydrogen and Oxygen in Fluidized Bed Reactor with Different Gas Distributors
PO-1-4-23	Kayo Sawada	Chlorination of antimony and its volatilization treatment for waste antimony-uranium composite oxide catalyst
PO-1-4-24	Jana Sulakova	A Study of 2.6-Bis[(Bis(2-N-Octyl)Phosphino)Methyl]Pyridine N,P,P'-Trioxide in Solvent Extraction of Actinides
PO-1-4-25	Chien M. Wai	Dissolution and Extraction of Uranium Dioxide using Ionic Liquid and Supercritical Fluid Carbon Dioxide

Subject Area 6 – Radioactive isotope beams

PO-1-6-1	Lisa Biasetto	Development of Porous Uranium Carbide for the SPES Project

Subject Area 7 - Actinide Science

PO-1-7-1	Takayuki Nagai	Absorption Spectra and Cyclic Voltammograms of Uranium Species in Molten Lithium Molybdate-Sodium Molybdate Eutectic at 550 C
PO-1-7-2	Tashi Parsons-Moss	Study of Actinide and Lanthanide Complexation by Organically Modified Mesoporous Silica
PO-1-7-3	Dean R. Peterman	Evaluation of Covalent Interactions in Actinide Coordination Compounds
PO-1-7-4	P.K. Pujari	Thermodynamics of Th(IV) Complexation with Dicarboxylate Ligands: A Potentiometric and Calorimetric Study
PO-1-7-5	Tatsuya Suzuki	Adsorption Behaviors of F-Elements on Tertiary Pyridine and Quaternary Pyridiunium Resins
PO-1-7-6	Yoshinori Suzuki	Electrochemical studies on microbial U(VI) reduction
PO-1-7-7	Reona Takayama	Solvent Extraction of Trivalent Actinides with Di(2-Ethylhexyl) Phosphoric Acid and Thenoyltrifluoroacetone
PO-1-7-8	Akihiro Uehara	EXAFS analyses of Uranium(IV) and Thorium(IV) complexes in CaCl2*6H2O hydrate melt
PO-1-7-9	Xiao-qiu Ye	The Molecular Structure and Potential Energy Function of Li-M (M=Be, Pb, Bi, Th, U) Diatomic Molecule
PO-1-7-10	Takashi Yoshimura	Measurements of Mobility for Actinides and Lanthanides Using Capillary Electrophoresis, and its Application to Short-Lived Nuclides

Subject Area 8 - Environmental radiochemistry and radioecology

PO-1-8-1	Claudine Armenta	Rapid Environmental Analysis Using Molten Salt Fusion Sample Preparation
PO-1-8-2	M. Lee Davisson	The Low-Level Radioactive Waste Disposal Site of Runit Dome on Enewetak Atoll, Marshall Islands: Its History, Construction, and Need for Characterization and Monitoring
PO-1-8-3	Nick Evans	Aspects of radionuclide chemistry in the near field of a cement-based ILW disposal concept in the UK
PO-1-8-4	Taijiro Fukuyama	Distribution coefficient of 7Be in overland flow along a forested hillslope: field measurements and laboratory batch experiments
PO-1-8-5	Etsuko Furuta	Classification of ores used for the radiation source in NORM by PGAA
PO-1-8-6	Muhammad Ismail	Radioactivity in vegetation, vegetable and transfer of radionuclides from soil to vegetation of some Northern area of Pakistan using gamma ray spectrometry
PO-1-8-7	Nao Kamei-Ishikawa	Relationships Among 137Cs, 122Cs, and K in Plant Uptake Observed in Japanese Agricultural Fields
PO-1-8-8	Hasan Mahmood Khan	Assessment of radionuclies, trace metals and radionuclides transfer from soil to food of Jhangar Valley (Pakistan) using gamma spectrometry
PO-1-8-9	Yoshikazu Kikawada	Origin of enriched uranium contained in Japanese atmospheric deposits
PO-1-8-10	Takumi Kubota	Comparison of Deep Underground Neutron Flux Measured with a Helium-3 Filled Proportional Counter and Evaluated from Element Composition or the Isotopic Ratio of 36Cl/Cl in Granite Rock
PO-1-8-11	Tom Lonnoth	Study of the 7Be and137Cs Activities in Mushrooms from Southern and Western Finland
PO-1-8-12	Galina Lujaniene	Plutonium Oxidation State Distribution in Natural Clay Systems: Effect of Iron Oxides and Microorganisms
PO-1-8-13	Galina Lujaniene	Study of Pu(IV) and Am(III) Sorption to Clay Minerals
PO-1-8-14	Seiya Nagao	Molecular Sized Dependency of Am Complexed with Humic and Fulvic Acids in Groundwaters with High DOC Concentration
PO-1-8-15	Yuichi Oki	Radioactive Aerosol Particles Released from a Pneumatic Irradiation System in a Nuclear Research Reactor
PO-1-8-16	Naoyuki Osada	Application of Graded Screen Array to Size Measurement of Radioactive Aerosol in Accelerator Rooms
PO-1-8-17	P.K. Pujari	Study on Aggregation Behavior of Humic Acid: Effect of pH and electrolyte
PO-1-8-18	Yamauchi Rieko	Depleted Uranium Found in the Reference Fallout Material for Activity Measurements in Japan
PO-1-8-19	S.K. Sahoo	Determination of U Concentration and its Activity Ratio in Coal and Fly Ashes from Philippine Coal-Fired Thermal Power Plants Using ICP-MS and TIMS
PO-1-8-20	Keisuke Sueki	Isotope ratios of 36Cl/Cl in soils at the south Tohoku by AMS
PO-1-8-21	Hideo Sugiyama	Intake of Po-210 and K-40 from the total daily diet for adults in Japanese cities.
PO-1-8-22	Keiko Tagami	Rhenium Concentration Effect on Technetium Transfer Through Radish Roots and Rhenium Toxic Concentration Levels in Radish
PO-1-8-23	Tomoyuki Takahashi	Development and Analysis of a Dynamic Compartment Model to Predict Carbon-14 Behavior in Rice Paddy Field for Dose Assessment of Atmospheric Release
PO-1-8-24	Punam Thakur	Environmental Monitoring of Radioactive and Non-Radioactive constituents in the vicinity of WIPP- A CEMRC Perspective
PO-1-8-25	Shigeo Uchida	Iodine Transfer from Agricultural Soils to Edible Part of Crops
PO-1-8-26	Paitoon Wanabongse	Measurement of radon gas, gamma-ray exposure and some naturally occurring radionuclides.
PO-1-8-27	Masato Yamawaki	A Study of 32P-Phosphate Uptake in a Plant Using a Real-Time RI Imaging System
PO-1-8-28	Mavrik Zavarin	Interaction of Plutonium with Montmorillonite: Surface Complexation and Ion Exchange

Poster Session II – Tuesday, December 1, 2009 – 5:30 – 8:30 PM

Subject Area 3 - Radiation Detection: Radiation dosimetry and metrology

PO-2-3-1	Yoshimune Ogata	Estimation of Thermal Neturon Flux in PET Cyclotron Rooms by means of Radioactive Analysis of Bolts in the Rooms
PO-2-3-2	Koichi Takamiya	A New Preparation Method for Neutron Monitor Using Ink-Jet Printer
PO-2-3-3	Hiroshi Yasuda	Dosimetry of Cosmic Radiation in the Upper Atmosphere Based on the Measurements at the Summit of Mt. Fuji

Subject Area 5 - Nuclear reactions, nuclear decay/structure/cross sections, nuclear fission, heavy and super heavy elements science

PO-2-5-1	Daniel Cummings	Advancements in Burn-Up Measurements by Inductively Coupled Plasma Mass Spectrometry
PO-2-5-2	Parnika Das	Change of Electron Capture Decay Rate in a Compact Medium
PO-2-5-3	Roger Henderson	Recent Developments in Heavy Element Separation Methods Using DGA Resin
PO-2-5-4	Daiya Kaji	Preparation of 248Cm Target from Old 252Cf Neutron Source
PO-2-5-5	Daiya Kaji	Average Equilibrium Charge States of Superheavy Recoil Ions Moving a Dilute Helium Gas
PO-2-5-6	Kentaro Hirose	Precision Measurement of the Half-Life of 196Au and 202Tl
PO-2-5-7	Hidetishi Kikunaga	Precision Measure of the Half-Life of 90mNb and 99mTc
PO-2-5-8	Yukiko Komori	Development of an On-Line Liquid Scintillation Alpha Particle Detection System for Aqueous Chemical Studies of Superheavy Elements
PO-2-5-9	Yuichiro Nagame	Chemical Equilibrium in Atom-at-a-time Chemistry
PO-2-5-10	Ichiro Nishinaka	Radiochemical Study of Sub-Barrier Fusion Hindrance in 19F+209Bi Reaction
PO-2-5-11	Takashi Omoto	Cross-Section Measurements for Monoenergetic Neutron-Induced Reactions at RCNP
PO-2-5-12	Kazuhiro Ooe	Extraction Behavior of Carrier-Free and Macro Amounts of Molybdenum and Tungsten from HCl Solution
PO-2-5-13	Alexander A. Plionis	Improved Nuclear Data Measurements of Alpha-Emission Branching Ratios by Ultra-High Resolution Microcalorimetry
PO-2-5-14	P.K. Pujari	Complete and Incomplete Fusion in 9Be + 124Sn System
PO-2-5-15	Tetsuya K. Sato	Development of an On-Line Isothermal Gas Chromatographic Apparatus for Db and Sg
PO-2-5-16	S. Sekimoto	Measurements of Be-10 and Al-26 Production Cross Sections for Cr, Y, and Yb with 285 MeV Neutron
PO-2-5-17	Tarkeshwar Trivedi	Lifetime Measurement of High Spin States in 75Br Through Doppler Shift Attenuation Method
PO-2-5-18	Hiroshi Yashima	Measurements of the neutron activation cross sections for Bi at 300 and 400 MeV
PO-2-5-19	Akihiko Yokoyama	Study on the Synthesis of Heavy Elements Through Nuclear Fusion Induced by Oxygen-16 on Rare Earth Targets

Subject Area 4 - Nuclear energy chemistry, the Global Nuclear Energy Partnership (GNEP), and Global Warming: Fuel reprocessing and new separation process; nuclear waste management and disposal; nuclide migration and performance assessment of geologic (high-level) nuclear repositories

PO-1-4-20	Yasuhisa Oya	Dynamics of energetic hydrogen isotopes in carbon-related materials for fusion reactor application

Subject Area 9 - Nuclear Analytical techniques: Neutrons; Ions; X-ray; Synchotron radiation, etc.

PO-2-9-1	Amares Chatt	An Analytical Figure of Merit (AFOM) Factor For Evaluating Advantages of Anticoincidence Gammy-Ray Spectrometry in Neutron Activation Analysis
PO-2-9-2	Juan F. Facetti-Masulli	Selected trace and minor elements of bottom sediments from Acaray Reservoir
PO-2-9-3	Jun Furukawa	Quantitative Trait Locus Analysis for Seed Zinc Accumuluation in Model Legume, Lotus Japonicus
PO-2-9-4	Jong-Myoung Lim	Characteristics of the Trace Elements in Indoor PM10 and PM2.5 at Subway Station Using Neutron Activation Analysis
PO-2-9-5	A. A. Naqvi	Optimization of Performance of a Channel Moderator of a PGNAA Setup for Carbon, Nitrogen and Oxygen Detection
PO-2-9-6	Takahito Osawa	Preliminary Research for Iridium in Cretaceous-Tertiary Boundary Clay Using Multi-Gammy Ray Detection
PO-2-9-7	Gwang-Min Sun	Application of Instrumental Neutron Activation Analysis for Examination of Oil Pigments
PO-2-9-8	Gwang-Min Sun	Determination of Degradation Constant of Li Ion from 10B 7Li reaction in Various Media
PO-2-9-9	Diandou Xu	Hybrid Neutron Activation Analysis for Study of Organic Halogens in Precipitation in Beijing, China

Subject Area 10 - Radiopharmaeutical chemistry, including Tc chemistry, nuclear imaging, and radioisotope production

PO-2-10-1	Sima Attar Nosrati	Evaluation of synthetic conditions of zirconium molybdate gel for use in the 99Mo/99mTc generators
PO-2-10-2	Yutaka Ezaki	Production of Rare Earth Multitracer from natHf with 125-MeV/Nucleon 14N Ions
PO-2-10-3	Sandrine Huclier-Markai	Evaluation of Gallium Polyaminopolycarboxylate Complexes
PO-2-10-4	Noriko Ishioka	Synthesis and Evaluation of Br-76 Labeled Glucose for Tumor Diagnosis with PET
PO-2-10-5	Shigeki Watanabe	Synthesis of 77Br Labeled Phenylalanine: A Preliminary Investigation for the Preparation of Radiobromine Labeled Peptide

Subject Area 11 - Applications of nuclear & radiochemical techniques in Life Science; Nano Science; Environmental Science; Geo-and Cosmo sciences, Archaeology; etc.

PO-2-11-1	Pisutti Dararutana	A XANES Study on Ancient Thai Glass
PO-2-11-2	Maria do Carmo Freitas	Air Pollution in chemical Elements, Determinied by INAA, and Childhood Leukaemia in Portugal
PO-2-11-3	Maria do Carmo Freitas	Analysis of Air Particulate Matter in Teflon and Quartz Filters by Short-Irradiation, Epithermal-Neutron Activation with Compton Suppression
PO-2-11-4	Maria do Carmo Freitas	Characterisation of Biomonitors Used in Metal Air Pollution Studies: Capacity, pK-Values and Metal-Exchange Behaviour of *Parmelia sulcata*
PO-2-11-5	Maria do Carmo Freitas	Characterisation of Soils, Plants, and Water Samples Collected at Sao Domingos Mine, Portugal
PO-2-11-6	Mitsuru Ebihara	Application of NAA to the Trace Elemental Determiniation for Nail Samples from Residents of Tokyo, Japan
PO-2-11-7	Mitsuru Ebihara	Determination of ultra-trace rare earth elements in ureilite meteorites by radiochemical neutron activation analysis with an emphasis of the correction for the contribution caused by neutron-induced fission of uranium
PO-2-11-8	Mitsuru Ebihara	Cosmogenic Sc-45 in Gibeon Iron Meterorite by Radioanalytical Neutron Activation Analysis
PO-2-11-9	Toshiyuki Fujii	Mass-Dependent and Mas-Independent Isotop Fractionations of Lead in Chemcial Exchange Reaction Using a Crown Ether
PO-2-11-10	Satoshi Fukutani	Study on Antimony Pollution Form in Soil Around Smelter by means of INAA
PO-2-11-11	Etsuko Furuta	Heavy metal elements in toiletries analyzed by INAA and ICP-MS
PO-2-11-12	Xiao He	Deposition in Lung and Translocation to Secondary Target Organs AfterIntratracheal Instillation of Nano-Ceria
PO-2-11-13	Inaya Lima	Investigation of minerals distributions in bone of tibolone therapy by Synchrotron X-Ray Fluorescence Microscopy
PO-2-11-14	Inaya Lima	The Zinc Distribution in Bone
PO-2-11-15	Mutsuo Inoue	Vertical Distributions of 228Ra and 226Ra in the Japan Basin; Implications for Water Circulation and Residence Time
PO-2-11-16	Satish Kayasth	Separation Science and Instrumental Approaches in Radioanalytical Chemistry
PO-2-11-17	Yoko Kokubu	Application of continuous heating method by thermal ionization mass spectrometry for measurement of isotope ratios of plutonium and uranium in trace amount of MOX sample
PO-2-11-18	Myung-Ho Lee	Isotope Correlations for Alpha Specific Activity and Isotopic Composotion of Plutonium in High Burn-Up Pressureized Water Reactor Samples
PO-2-11-19	Jong-Myoung Lim	Elemental Analysis of Fly and Bottom Ashes from a Coal Power Plant by Neutron Activation Analysis
PO-2-11-20	Yukihiro Murakami	Measurements of detection limits for trace elements by multiple prompt gamma-ray analysis
PO-2-11-21	Kevin Norbash	Reprocessing of Research Reactor Nuclear Fuel Based on Pyrochemical Separations Technique
PO-2-11-22	Shin-ichi Sawada	Water diffusion in fluoropolymer-based fuel-cell electrolyte membranes investigated by radioactivated-tracer permeation technique
PO-2-11-23	Keisuke Sueki	Synthesis of water-soluble encapsulated-radioisotope fullerenes
PO-2-11-24	Shinji Sugihara	The Extraction of Past Environmental Information Using 137Cs and Some elements in Terrestrial Carbonate Deposits
PO-2-11-25	Gwang-Min Sun	Development of Classification Technology for the Characterization of Raw Materials at Production Kilns in Baekje Period
PO-2-11-26	Naruto Takahashi	Preparation of Labeled Prophyrin Compounds for PET and Gamma CT
PO-2-11-27	Junpei Tomita	Ra isotopes in Na-Cl type groundwaters from deep wells in the coastal areas of Himi City, Toyama Prefecture, Japan
PO-2-11-28	Tong-Zai Yang	Structural Change of Multiwalled Carbon Nanotubes Through X-Ray Irradiation
PO-2-11-29	Hiroya Yokoyama	Meteorological Factors Producing Variation of Tritium Concentrations Measured in Fukuoka, Japan
PO-2-11-30	Hong Zhang	Cyclic Neutron Activation Analysis of Fluorine in Commericial Tea at Shenzhen, China
PO-2-11-31	Zhiyong Zhang	Radiotracer Technique: A Useful Tool for Studies of the Environmental Behavior of Nanomaterials

Subject Area 12 - Nuclear probes for new materials: Mossbauer; perturbed angular correlations; positron annihilation, etc.

PO-2-12-1	Kiyoshi Nomura	Characterization of 57Fe implanted SnO2 films by Mossbauer spectroscopy and Nuclear Inelastic Scattering.
PO-2-12-2	Kiyoshi Nomura	H/D Isotope Effect and Magnetic Properties of Cyanide-Bridged Nd(III)-Fe(III) Complex
PO-2-12-3	P.K. Pujari	Positronium Chemistry in Nanodroplets
PO-2-12-4	Yasuhiro Yamada	In-Beam Mossbauer Spectroscopy of 57Mn Implanted Into Aluminum Oxide
PO-2-12-5	Yasuhiro Yamada	In-Beam Mossbauer Spectroscopy of 57Mn Implanted Into Magnesium Oxide
PO-2-12-6	Yasuhiro Yamada	Laser Deposition of Iron in Oxygen Atmosphere
PO-2-12-7	Akihiko Yokoyama	Local fields at impurity sites in ZnO

ABSTRACTS: Plenary, Topical, and Submitted Oral Presentations

ROLE OF THE PERIODIC TABLE IN THE DISCOVERY OF NEW ELEMENTS

Darleane C. Hoffman

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Berkeley, CA 94720, USA

This year marks the 140th Anniversary of Mendeleev's original 1869 periodic table of the elements which was based on atomic weights rather than atomic numbers. The history of the development of chemical periodic tables will be outlined and the roles they played in the discovery of new chemical elements will be considered. The value as well as the sometimes negative effect on the prediction of the chemical properties of new elements will be pointed out. Glenn Seaborg's 1945 periodic table [1] showing placement of an actinide series underneath the lanthanide series in the periodic table had a tremendous influence on the search for new elements beyond neptunium and plutonium and resulted in the prompt discovery of americium and curium by his group in 1944-45.

The question will be explored as to whether or not there will be a future role for the periodic table in predicting chemical properties as we approach element 118 and perhaps go beyond to a new "g-block" of elements where relativistic effects (that increase roughly as atomic number squared) will make simple extrapolations from known properties meaningless. Furthermore, the half-lives of new elements and their production rates are continuing to decrease. Mendelevium (Z=101) is the heaviest element so far to be discovered by chemical rather than nuclear or physical techniques. So the question remains "What is the future role of the periodic table?"

[1] The Chemical and Radioactive Properties of the Heavy Elements, G. T. Seaborg, Chem. & Eng. News, **23**, 2190-93, Dec. 10, 1945

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HOW MUCH ENERGY DO WE NEED FOR A JUST AND SUSTAINABLE FUTURE?

James L. Conca[1], Judith Wright[2]

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The United States is at a crossroads in its economic and national security that will determine our strength and leadership at home and in the world for the next century. The same can be said for almost every other nation on Earth. This critical point involves our sources of energy, both their quantity and quality. Energy has always been directly tied to quality of life for humans. The United Nations Human Development Index calculates that about 3,000 kWhrs per person per year is necessary for a good life. Evaluating present usage among developed and developing worlds, using a projected population growth to about 9.5 billion by mid-century, and factoring projected gains in efficiency and conservation, the world will require about 30 trillion kWhrs per year by about 2040 if the world is to attain global peace and prosperity in this century.

Since we are presently at 15 trillion kW-hrs/year, this doubling of energy consumption will be difficult to obtain without a dramatic increase in fossil fuel use and its consequences, e.g., CO_2 emissions and the effects on ocean pH and climate change, environmental degradation from mining, water and air pollution, and health care costs generated from upper respiratory effects. And because most of this accelerating growth in energy consumption is occurring in developing countries, changes within the United States will have little effect unless it is to lead the world in replacing coal and oil by the new designs for alternative energy systems.

Since all fossil fuel use today generates 10 trillion kW-hrs/yr world-wide, if we level consumption at 30 trillion kW-hrs/yr without increasing CO_2 levels much above the present (about 380 ppm), then two-thirds of production must come from non-fossil fuels, and only one-third can come from fossil fuels. But this means that fossil fuel production will continue on at present rates, and not decrease as is assumed by Kyoto-type protocols. Instead of cutting production, increased efficiencies, carbon sequestration and other advances will have to be used to reduce CO_2 levels below those of today.

A target distribution, or energy mix, that would provide two-thirds of the world energy consumption from non-fossil fuels is about $^1/_3$, $^1/_3$, $^1/_3$: a third fossil fuels, a third renewables and a third nuclear. This $^1/_3$, $^1/_3$, $^1/_3$ distribution assumes that biofuels from high-efficiency biomass will provide almost as much automobile fuel as is presently provided by petroleum, in absolute volume, and assumes that sufficient Gen-III+ nuclear reactors are constructed to produce baseload electricity for plug-in vehicles or hydrogen for fuel cells. Both are achievable. The main hurdle to developing renewables to this degree is obtaining materials such as steel, copper, cement and semi-precious metals. The main hurdle to developing nuclear to this degree is the lack of global inter-nation partnerships such as world fuel banks, international spent fuel and waste take-back programs, and centralized geologic repositories.

The lesson here is that we are being too timid in our plans for developing non-fossil fuel energy sources, and this lack of urgency will condemn us to a greatly expanded use of conventional and unconventional fossil fuels and technologies such as coal-to-gas, gas shales and tar sands. Achieving this $^1/_3$-$^1/_3$-$^1/_3$ mix requires committed leadership amongst the nations of the world, with an understanding that failure will result in developed nations losing their high standards of living and developing nations losing the opportunity to achieve such standards, while the planetary ecosystem teeters on the brink of collapse.

ACTINIDE SEPARATIONS IN THE U.S. ADVANCED FUEL CYCLE INITIATIVE

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The Department of Nuclear Energy's Advanced Fuel Cycle Initiative (AFCI) is developing actinide separation technologies in support of future sustainable fuel cycles. One of the driving forces behind separating actinides from used nuclear fuel is to reduce the time that used fuel or waste products will require isolation from people. Currently, the radiotoxicity of used fuel is higher than that of natural uranium ore for hundreds of thousands of years. By separation and transmutation of actinides (Np, Pu, Am) the radiotoxicity of used fuel can be reduced to that of uranium ore in several hundred years.

This means that the majority of the used fuel can be managed on engineering time scales, rather than geologic time scales. The small remainder of long-lived fission products, primarily ^{129}I, ^{99}Tc, and ^{135}Cs, have very long half lives, but have relatively low radiotoxicity. These will require new technologies to transmute them or isolation for very long (millions of years). The AFCI program is researching new methods to separate actinide elements, including modifications to TBP-based extraction processes, new extraction processes, and electrochemical separation in molten salt. An update of recent research activities, will be presented as well as a discussion of new program direction to include more science based research into the program.

1-PS7 17346

INVESTIGATIVE RADIOCHEMISTRY – A KEY ELEMENT IN NUCLEAR FORENSICS

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Since the fall of the iron curtain illicit trafficking of nuclear and radioactive material has become an issue of concern both on the political and the scientific level. Seized material has to be analysed in order to obtain clues on its origin and intended use and to prevent diversion of nuclear material from the same source in the future. Nuclear materials (uranium or plutonium) are of particular interest due to the proliferation associated with the material. Nuclear forensic investigations are based on the fact that nuclear material carries (inherent) information on its history, thus on its origin and the processes applied for its production. Important conclusions can be drawn from decay products, activation products or fission products. Chemical impurities and the isotopic composition of certain major and minor constituents may provide additional information. Material properties, like density, porosity, surface roughness or grain size distribution can also be helpful for attributing seized material to a certain process or origin. Comparison of the measured results with nuclear material databases may yield evidence on the production site. The paper will describe the methodologies developed for addressing the above issues, focussing on radiochemical methods. Examples of nuclear forensic casework will illustrate the experience gathered in these areas. Finally, an overview on current technical developments will be provided.

1-PS8 22534

THE RELEVANCE OF RADIOACTIVE PARTICLES IN THE ENVIRONMENT

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Following a series of serious nuclear and radiological events during the last 60 years, a major fraction of refractory radionuclides such as uranium and plutonium has been released into the environment in the form of radioactive particles. These entities can carry a substantial amount of the bulk radioactivity, are inhomogeneously distributed in the environment, and representative sampling can be difficult to attain. Particles can be difficult to dissolve and partial leaching can result in underestimation of the inventory. Radioactive particles can also act as point sources and may contribute to significant doses when retained in biological tissues. Soils and sediments can act as an intermediate sink for radioactive particles, and the ecosystem transfer will be delayed if radioactive particles are present. Due to particle weathering, however, associated radionuclides can be mobilized over time. Thus, contaminated soils and sediments can act as a diffuse source of particle-associated radionuclides in the future. Thus, information on particle characteristics influencing weathering and remobilisation of associated radionuclides as well as biological uptake and effects is essential in environmental impact and risk assessment.

Radioactive particles released from different nuclear sources such as nuclear weapon tests (Semipalatinsk), nuclear accidents (Chernobyl, Windscale, Thule, Palomares), and nuclear reprocessing plants (Mayak, La Hague, Sellafield, Dounreay) have been characterised using solid state speciation techniques. The techniques have also been applied to particles released from depleted uranium ammunitions (Kosovo, Kuwait), from radioactive waste dumped at sea (Kara Sea), and from uranium mining and tailing sites (Central Asia). Based on scanning electron microscopy (SEM) combined with synchrotron radiation x-ray micro-techniques, and mass spectrometry, particles are characterized with respect to variables influencing particle weathering processes and ecosystem transfer; size, composition, morphology, structure, and oxidation states of the carrying matrix. The results show that the composition of radionuclides in particles is source-related, while particle characteristics related to structures and oxidation states also depend on release conditions. The work demonstrates also that radioactive particles and colloids have been released from a series of sources in the past, more frequently than usually anticipated, and that particles should be expected if refractory radionuclides are identified in the environment.

LEGACY OF URANIUM EXTRACTION AND ENVIRONMENTAL SECURITY IN THE CENTRAL ASIAN REPUBLICS OF KAZAKHSTAN, KYRGYZSTAN, TAJIKISTAN AND UZBEKISTAN

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Uranium ore mining and processing started in the former Soviet Republics of Kazakhstan, Kyrgyzstan, Tajikistan and Uzbekistan after the Second World War and lasted for almost half a century. Extensive mining and milling activities resulted in large amounts of uranium tailing materials and waste rock deposits, often dumped in inhabited areas or in their close vicinity. Both materials may have a potential radiological impact on the environment and local populations.

A NATO Science for Peace (SfP) project to secure the effective management of uranium industry wastes in the Central Asian republics of Kazakhstan, Kyrgyzstan, Tajikistan and Uzbekistan in order to prevent health and environmental damage, has begun in 2006. The participating institutions include Jožef Stefan Institute, Slovenia, Joint Stock Company Volkovgeologiya and Al-Farabi Kazakh National University from Kazakhstan, Chu Laboratory of Ecology, Kyrgyzstan, State Owned Company Vostokredmet, Tajikistan and the Institute of Nuclear Physics, Uzbekistan.

The research part of the project is associated with radiological assessment of uranium sites using modern equipment, survey methods and protocols. The application of relevant analytical methods and techniques for studying the behaviour of naturally occurring radionuclides at the source of radioactivity and in the environment, such as their pathways, migration, accumulation, represents the main research component of the project. It extends to utilization of methods, models and protocols for radiation dose and risk assessments on the potentially exposed human population, as well as for establishing appropriate mitigation/remediation countermeasures to minimize the impact on the environment and resident populations.

Work related to this SfP project was carried out in three phases: characterization of source-terms and determination of local contamination at selected uranium tailing sites; radiation dose and impact assessment; identification of appropriate mitigation/remediation countermeasures.

The results obtained so far showed that radiation doses to resident populations at practically all of the investigated sites (Kurday, Kazakhstan, Shekaftar, Min-Kush, Kadji Sai, Kyrgyzstan, Taboshar and Digmay, Tajikistan, Yangiabad and Chorkesar, Uzbekistan) were low. No radiological risk and no actual health impact on resident public can be expected. Radiation at the sites is localized and has no or very little influence/impact on broader areas such as Ferghana Valley. However, specific radiological situations, i.e. in Taboshar, Digmay and Min-Kush, should be addressed adequately, in order to protect members of the resident public by applying appropriate remediation countermeasures.

2-S8-2 16301

SORPTION OF EU(III) ON ATTAPULGITE, ZSM-5 AND MWCNTS: STUDIED BY BATCH, XPS AND EXAFS TECHNIQUES

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The sorption of Eu(III) on attapulgite, ZSM-5 and MWCNTS was investigated using batch, X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) techniques in detail. The results indicated that the sorption of Eu(III) on these 3 materials was strongly dependent on pH and ionic strength. In the presence of FA/HA, Eu(III) sorption to attapulgite was enhanced at pH < 4, decreased at pH 4-6, and then increased again at pH > 7. The sorption edges of Eu(III) to ZSM-5 could be modeled in the pH range ~3 to ~10 using cation exchange reactions for Eu^{3+}/Na^+ and three surface complexation reactions on the sorption sites forming =SOEu, $=SOEu(OH)^+$ and $=SOEu(OH)_2^0$ inner sphere complexes appear successively with increase of pH. The presence of HA enhances Eu(III) sorption to HA-MWCNT hybrids. The XPS analysis suggested that the Eu(III) sorption to attapulgite might be expressed as $\equiv X_3Eu^0$, $\equiv S^wOHEu^{3+}$ and ≡SOEu-OOC-/HA in the ternary Eu/HA/attapulgite system; and the functional groups of HA contribute to Eu(III) sorption to MWCNTs. The EXAFS analysis of Eu-HA complexes indicated that the distances of d(Eu-O) decreased from 2.451 to 2.360 Å with increasing pH from 1.76 to 9.50, whereas the coordination number (N) decreased from ~9.94 to ~8.56. Eu(III) sorption to ZSM-5 could be simulated (R=0.045) by assuming a number of oxygen N=7.7(5) at d(Eu-O)=2.31Å (σ =0.01Å), the species of Eu(III) adsorbed on ZSM-5 surface were obviously different from the species of Eu(III) in aqueous solution. (Figs. 1 and 2).

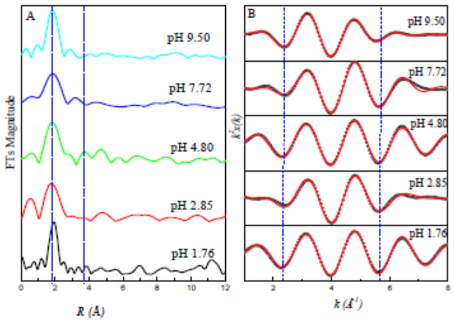

Figure 1. The corresponding Fourier Transforms (A) and the first-shell fit of the EXAFS function of k^2-weighted (B) of the binary Eu/HA system at different pH values. A: Eu L_{III}-edge EXAFS spectra of FTs magnitudes; B: Experimental (open circles) and model (solid line) Fourier-filtered $k^2\chi(k)$ contribution for the next-nearest backscattering shells at R distances spanning the [1.3, 2.9 Å] interval.

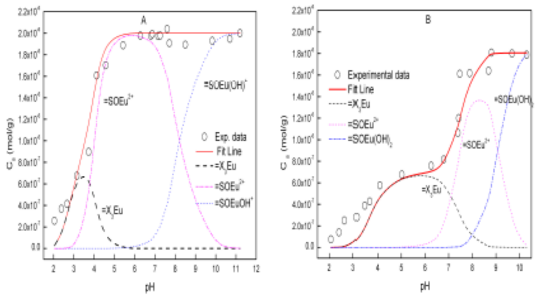

Figure 2. The distribution species of Eu(III) in ZSM-5 zeolite suspension. m/V =0.5g/L; T=25±2 °C; $C[Eu(III)]_{initial}=1\times10^{-6}$ mol/L. A: I=0.01 mol/L $NaClO_4$, CCM; B: I=0.1 mol/L $NaClO_4$, CCM.

A COMPARATIVE COMPLEXATION STUDY ON Np(V) INTERACTIONS WITH BACTERIAL CELL WALL COMPARTMENTS AND BIOLIGANDS SECRETED BY MICROBES

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Microorganisms, microbial components, biopolymers and bioligands secreted by microbes have a great potential to influence the behavior of actinides in the environment. Functional groups provided by both lipopolysaccharide (LPS: main part of the cell wall of Gram-negative bacteria), and peptidoglycan (PG: main part of the cell wall of Gram-positive bacteria) are very effective in complexing uranium(VI) over a wide pH range (2.0 to 9.0) [1, 2]. The main functionalities for uranyl binding are phosphoryl and carboxyl groups of LPS and carboxyl groups of PG. The aerobic soil bacterium *Pseudomonas fluorescens* (CCUG 32456 A) isolated from the aquifers at the Äspö Hard Rock Laboratory, Sweden secretes pyoverdins. These unique bioligands have a high potential to bind uranium(VI) and curium(III) mainly due to their hydroxamate and catecholate functionalities [3, 4]. However, the interaction of neptunium(V) with both microbial cell wall components (LPS, PG) and secreted bioligands (PYO) are unknown. To address this lack, we thus present findings regarding the complexation of neptunium(V) with LPS, PG, and *P. fluorescens* (CCUG 32456) pyoverdins (PYO) obtained using near-infrared (NIR) absorption spectroscopy.

The spectrophotometric titrations of the Np(V)−LPS system showed a dominant neptunyl(V) coordination to phosphoryl groups between pH 4 and 8 followed by hydroxyl interactions in the alkaline pH range. A very low affinity of Np(V) to interact with the carboxyl groups of PG was measured. Strong NpO_2^+−pyoverdin species of the type $M_xL_yH_z$ could be identified from the spectrophotometric titrations. Remarkable was that the influence of Np(V)−pyoverdin species could already be detected under equimolar conditions.

Estimates are possible, on the basis of the determined stability constants, if neptunium(V) prefers to interact with the microbial cell wall (LPS), with biopolymers (PG) or with the secreted pyoverdin bioligands (PYO). The calculations were performed using nearly equimolar conditions of Np(V) and functional groups of the biosystems. More than 80% of all Np(V) is bound to pyoverdin species at pH 8 compared to ~37% bound to LPS and less than 1% bound to PG. This shows both the high affinity of neptunium(V) to bioligands containing hydroxamate and catecholate groups and the importance of indirect interaction processes between neptunium(V) and bioligands secreted by resident microbes.

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ASPECTS OF THE COMPLEXATION OF Tc(IV) WITH ORGANIC LIGANDS IN UK RADIOACTIVE WASTE DISPOSAL

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The preferred UK option for the management of intermediate-level radioactive waste is to store it in a deep Geological Disposal Facility (GDF). This may then be backfilled with a cementitious material. Once closed, the GDF will become saturated with groundwater, and highly alkaline porewater will develop with an initial pH of *ca.* 13.4. This will decrease to 12.5 as the groundwater flow dissolves, and removes, any NaOH and KOH present. The mineral phases in the cement will act as a buffer and maintain the pH at 12.5 for *ca.* 10^5 years. Corrosion of waste-containing steel canisters will lead to the gradual formation of reducing conditions. Thus, the behaviour of radionuclides in the waste must be understood in the context of this chemistry. In the past in the UK, small amounts of Tc were discharged into the sea. It was originally thought to disperse widely, but was discovered to concentrate in seaweed. Hence, treatment with tetraphenylphosphonium bromide (TPPB) is now used to precipitate out Tc, to prevent marine discharges. This leads to the possibility that the floc may be sent to a cementitious GDF. However, TPPB degrades by alkaline hydrolysis at high pH. It is also prone to radiolytic degradation. Organic complexing agents will be present as inherent components of the waste, especially those like isosaccharinic acid (ISA), gluconic acid and similar polyhydroxylated carboxylic acids which will be formed by the anaerobic, alkaline degradation of cellulose. These are highly complexing and can cause significant increases in radionuclide solubility at high pH. The GDF will not be homogenous, there are likely to be areas of reducing and oxidizing potential. This heterogeneity could mean that both Tc(VII) and Tc(IV) are present within the GDF. If TcO_4^- migrates into an area in which reducing conditions exist, the organics may complex with technetium during reduction to form water-soluble complexes. Also of relevance is the possibility of increased solubility when organics are in contact with reduced technetium (TcO_2(am)). In other words, does the presence of organics affect the reduction of Tc(VII) to Tc(IV)? With these considerations in mind, studies have been undertaken in which TcO_4^- was reduce electrochemically, and by use of Sn(II) and Fe(II), in the presence and absence of ISA, gluconic acid, EDTA, NTA and picolinic acid, to determine whether they caused an increase in Tc solubility when TcO_2(am) was contacted with them.

In the presence of ISA and gluconic acid a lowering of [Tc(aq)] took place on reduction, showing such ligands did not prevent reduction occurring. If this reduction was to Tc(IV), then the final aqueous concentration should be the same as that produced by the addition of the same ligands to Tc(IV) solution, i.e. the Tc(IV)-ligand complexes would again be formed, but by two different routes, assuming steady state had been obtained. However, the final Tc solubility in the system where reduction took place in the presence of gluconate was higher than when TcO_2 was the starting point. This indicates that Tc(VII) may not have been reduced to Tc(IV) but an intermediate oxidation state complex such as Tc(V) may have been formed. This idea is well known in the formation of ^{99m}Tc radiopharmaceuticals. It is known that polyhydric complexes of Tc(V) can be formed by the reduction of pertechnetate in aqueous solution of excess O-donor ligand, although in pharmaceuticals this is not carried out at high pH. Apart from a few cases, the complexes have not been structurally characterised, because of the difficulty of obtaining pure compounds in crystalline form.

RADIOCARBON OF AQUATIC HUMIC AND FULVIC ACIDS IN THE CHIKUGO RIVER WATERS

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Humic substances are a heterogeneous mixture of organic materials with wide range of molecular sizes. They are the largest fraction of dissolved organic matter in natural waters and act as a complexing ligand for trace elements in aquatic environments. The characteristics of aquatic humic and fulvic acids are important to understand the sources and dynamics of aquatic humic and fulvic acids in river systems. This study reports the downward trend in Δ^{14}C and δ^{13}C of dissolved humic and fulvic acids isolated from river waters along the Chikugo River, which is located in Kyushu Island in Japan.

The humic substances were isolated from 5.3 to 18.8 ton of the river waters at five stations from the upper to lower Chikugo River, which is 143-km long and 2863 km^2 of watershed, using the XAD extraction method on November 7–11 in 2005. The percentage of fulvic acid is 70±5% to total humic substances. Stable carbon isotopic ratio is determined by mass spectrometry and is reported in δ^{13}C notation versus the VPDB standard. Radiocarbon in humic samples was determined using accelerator mass spectrometry at the Japan Atomic Energy Agency. Radiocarbon values are reported as Δ^{14}C corrected for sample δ^{13}C.

The Δ ^{14}C of dissolved humic and fulvic acids ranges from –64 to -15‰ and –35 to +20‰, respectively. The δ^{13}C values have –25.7to –23.6‰ for the humic acids and –27.3to –26.2‰ for the fulvic acids. The averaged values of Δ^{14}C and δ^{13}C are –39±18‰ and –25.0 ± 0.9‰ for the humic acids, respectively, and 8 ± 21‰ and –26.8 ± 0.5‰ for the fulvic acids. The Δ^{14}C and δ^{13}C values of fulvic acids are younger and lighter than those of humic acids. The Δ^{14}C of fulvic acids decrease from +20‰ in the upper site to –35‰ in the lowest site. The downward trend is similar with that of humic acids. The differences in Δ^{14}C between humic and fulvic acids at each site also decrease with increasing the distance from the upper stream. These results suggest that the supply of older humic and fulvic acids from watershed increase downward along the Chikugo River.

2-S8-6 16474

THE U.S. TRANSURANIUM AND URANIUM REGISTRIES: FORTY YEARS' EXPERIENCE AND NEW DIRECTIONS IN THE ANALYSIS OF ACTINIDES IN HUMAN TISSUES

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September 2008 was the 40th anniversary of the U.S. Atomic Energy Commission's vision in establishing the National Plutonium Registry. Its successors, the U.S. Transuranium and Uranium Registries (USTUR), continue to follow individuals with documented accidental exposures to actinide elements, to study their uptake, translocation and retention (biokinetics), and tissue dosimetry. To date, 330 past-worker volunteers have donated their tissues for scientific research, including 36 whole body donors. This talk outlines the history, mission and research goals of the Registries, and the current status of the USTUR's Radiochemistry Program. We present an overview of the analytical methods for plutonium (Pu), americium (Am) and uranium (U) isotopic determination in human tissues currently applied; including inductively coupled mass spectrometry (ICP-MS) based techniques. Recent developments in rapid radiochemical separation of the actinides from soft tissue and bone samples using vacuum-assisted extraction chromatography are also outlined. The results of inter-comparing $^{239+240}$Pu, ^{241}Am and ^{234,235,238}U determinations by ICP-MS, α-spectrometry (AS) and kinetic phosphorescence analysis (KPA, for total U) are discussed. ICP-MS is a major advance over AS and KPA in enabling the measurement of the ^{240}Pu/^{239}Pu atom ratio, the short-lived β-emitter ^{241}Pu, and the anthropogenic ^{236}U. For the first time ^{241}Am and ^{241}Pu were measured in human tissues using ICP-MS. The measured ^{240}Pu/^{239}Pu, ^{235}U/^{238}U and ^{236}U/^{238}U atom ratios clearly identify the origins of these actinides in human tissues. A new avenue of research with samples of USTUR human tissue is the application of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to elemental bio-imaging (EBI) of the actinides (of both anthropogenic and natural origin). We present elemental distribution maps for ^{235,238}U and ^{232}Th in lymph nodes measured for both non-exposed (chronic intake) and occupationally exposed (inhalation) subjects. The implications of these findings for dose assessment are discussed.

3-TS4-1 13499

CURRENT STATUS OF HIGH-LEVEL RADIOACTIVE WASTE DISPOSAL IN CHINA

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China plans to increase the share of the nuclear electricity from the current 2% up to 5% in the year of 2020. The fast development of nuclear energy will produce considerable amount of spent fuels and high level radioactive wastes and, the disposal of high-level radioactive waste in China is becoming one of the most pressing problems in terms of economic and political.

Beishan, in Gansu Province, Northwest of China, has been considered as one of the most important resaerch area for the potential geologic repository, and geologic survey, groundwater property investigation, drilling, radionuclide diffusion in Beishan Granite, mechanical property study of Beishan Granite have been carried in the past 10 years. Available data indicates that Beishan Granite is good as a host rock for the disposal of high level radioactive wastes.

The Wenchuan earthquake over scale 8 happened on May 12, 2008 reminds Chinese scientists thought that in terms of prohibiting the migration of radionuclides into the surroundings of a geologic repository, clay formation may has obverious advantages over granite, and the diffusion, migration characteristics of some important radionuclides in clay will be studied in the following 5 to 10years. In the following 10 years, more money will be investigated in the basic research including radionuclide migration, groundwater properties, material corrosion, thermodynamics of some radionuclides, colloid effects, and international information exchange.

Currently, the design of the underground laboratory is on the way and, the geologic survey for clay formations in China is being conducted.

ACTINIDE INTERACTION WITH GROUNDWATER COLLOIDS: SORPTION AT FEMTO- TO MICROMOLAR CONCENTRATION RANGE AND SURFACE COMPLEXATION MODELLING

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The PA of the nuclear waste repositories includes the studies of effects from colloids on radionuclide transport. The tendency to replace the Kd concept by the surface complexation modelling (SCM) for the radionuclide-colloid interactions is observed. The SCM is based on the calculation of the sorption equilibrium constants and by their combination with aqueous complex formation constants and solubility products, the Kd could be derived for any geochemical conditions. Despite the number of studies on sorption and SCM of actinides on different mineral phases were reported, the data are very dispersed or limited. This paper deals with the sorption and SCM exercises for the several experimental systems: U(VI), Pu(V) and Np(V) sorption onto amorphous silica, Pu(IV,V) sorption onto hematite and goethite and Np(V) sorption onto hematite, goethite, hydrous ferric oxide colloids separated from actual groundwater samples collected at the repository site. The experiments were done under well-defined laboratory conditions. The sorbat concentrations vary in the broad range – from femtomolar to micromolar range. For this purpose different isotopes were applied including short-lived Pu-237 (T1/2=45.6 d) and Np-239 (T1/2=2.36 d). In case of micromolar concentration of actinides, EXAFS was applied as a speciation tool and TRLIF in case of U(VI) sorption onto silica. SAXS was applied to detect the possible surface precipitation reactions of the actinides on the colloid surface.

For SCM various possibilities were considered including mono- and bidentate coordination while EXAFS data supported bidentate rather than minodentate complexation. The reduction of Pu(V) upon the interaction with Fe oxide colloids was established that result in the formation of precipitates on the colloid surface. For the first time the SCM of Pu(IV) sorption onto various colloids was performed at femto- and nanomolar concentrations that prohibit the formation of intrinsic colloids and polynuclear species.

3-S4-3 19170

THE DYNAMICS OF HEXAVALENT URANIUM SILICATE MINERAL DISSOLUTION AND SORPTION

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The uranyl silicate minerals are common in nature and very similar in structure and behavior to clay minerals. These include uranophane ($Ca[(UO_2)(SiO_3OH)]_2.5H_2O$), sklowdowskite ($Mg[(UO_2)(SiO_3OH)]_2$ $6H_2O$), and sodium boltwoodite ($Na(H_3O)[(UO_2)(SiO_4)]$), which are composed of negatively charged, two-dimensional sheets of uranyl cations coordinated to silicate anions. The threedimensional mineral structure is created by stacking the sheets and including the non-uranium cation shown in the chemical formulae in the interlayer space to balance the negative charge of the sheet. In aqueous suspensions, dynamic processes at mineral surfaces include sorption and desorption of dissolved metal cations, cation exchange in the interlayer, and possible dissolution of the mineral surfaces. Study of the kinetics of these processes allows possible elucidation of the mechanism(s) of these dynamic processes.

In this study, synthesized uranophane, sklowdowskite, and sodium boltwoodite were identified by powder x-ray diffraction and other methods. Uranyl sorption on these individual minerals was determined by batch method of suspensions using ^{233}U as a tracer. ICP-MS was used to determine dissolved uranyl. Uranyl sorption was measured as a function of pH and the mineral-to-metal ratio, in 0.1M $NaClO_4$ medium. Results showed minimal sorption at pH 6 and maximal retention above pH 8. Mineral dissolution and metal desorption was tested by first equilibrating mineral suspensions containing tracer levels of ^{233}U for 7 days at pH 11 where maximal sorption of the added U tracer is expected. Dissolution and desorption was initiated by lowering and buffering the system to pH 6 where desorption and possible dissolution are expected. Results show an initial mineral dissolution during the first 2 days of the experiment, followed by re-precipitation. ^{233}U desorption was observed during the first few days, but uranyl then re-sorbed on the minerals. These results will be discussed in the context of observed sorption behavior of other actinide cations such as NpO_2^+.

3-S4-4 21339

EXTRACTION PROPERTIES OF PODAND-TYPE NITROGEN DONOR LIGANDS TOWARD OXOANIONS

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Technetium (Tc) is the lightest chemical element with no stable isotope and exists as an oxoanion, pertechnetate ion (TcO_4^-), in an aqueous solution. A long-lived radioactive isotope, ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ years), whose nuclear fission yield is very high (about 6%), is one of the most hazardous contaminants, because of high water-solubility and bioavailability of TcO_4^-. Tc should be monitored in soil and water around nuclear reprocessing plants and recovered from the plants. Rhenium (Re) which is a non-radioactive congener of Tc is applicable as a substitute of Tc owing to their similar electronic configuration and stereochemistry and thermodynamic properties. In this study, ReO_4^- instead of TcO_4^- is used for all tests.

Coordination energy of the ligands with oxoanions has to be higher than the hydration energy of oxoanions. The use of encapsulating ligands, such as cryptands and podands, may be suitable for the establishment of oxoanions recognition system. These ligands may recognize oxoanions by both the electrostatic interaction between oxoanions and protonated ligands and the hydrogen bond formation, compared with simple open-chain ligands. *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)-1,2-ethylenediamine (TPEN) is one of the podand-type ligands. In this study, we test the extraction of ReO_4^- with TPEN and two TPEN analogs, *N*,*N*,*N'*,*N'*-tetrakis[4-(2-butyloxy)-2-pyridylmethyl]-1,2-ethylenediamine (TBPEN) and *N,N,N',N'*-tetrakis[4-(2-octyloxy)-2- pyridiylmethyl]-1,2-ethylenediamine (TOPEN).

For the extraction of ReO_4^- with TPEN, the percent extraction of Re increased with increasing acidity of the aqueous solution in the pH_{eq} range above 3.5 and decreased in the pH_{eq} range below 3.5. These results indicate that ReO_4^- is extracted as an ion pair with protonated TPEN in the lower acidic solution; but the extraction of ReO_4^- is reduced by the increase in the solubility of multi-protonated TPEN into the highly acidic solution. Two hydrophobic TPEN analogs introducing alkyl groups, TBPEN and TOPEN, were synthesized in order to suppress the dissolution of TPEN into the acidic solution. The percent extraction of Re for hydrophobic TPEN analogs increased with increasing acidity of the aqueous solution even in the pH_{eq} range below 3.5 and achieved approximately equal to 100% even at pH_{eq} 2.7. TOPEN was suitable for the extraction of ReO_4^- even at pH_{eq} 1.0. These results indicate that the improvement of hydrophobicity of ReO_4^--TPEN complex by the introduction of alkyl groups suppresses the dissolution of extractant into the aqueous phase and promotes the extraction of ReO_4^-. Note that the percent extraction of Re for TBPEN and TOPEN was also higher than that for TPEN in the pH_{eq} range above 3.5. It is presumed that the introduction of alkoxy groups which are electron-donating groups promoted the protnation of TBPEN and TOPEN.

TREATMENT OF RADIOACTIVE CONTAMINATED OILY WASTES USING ADSORPTION COUPLED WITH ELECTROCHEMICAL REGENERATION

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Adsorption coupled with electrochemical regeneration is a process for removing organic contaminants from water and wastewater, using a novel, non-porous, highly conducting, carbon adsorbent material, Nyex®. Whilst this process has been shown to be most cost effective when treating low and trace concentrations, it can also remove high levels of organic contamination from aqueous solutions where biological or other treatments are not feasible. Electrochemical regeneration is achieved through the anodic oxidation of the organics to carbon dioxide, carbon monoxide and water.

In this paper we report on the potential of this new process to treat low to medium level radioactive oil waste, generated principally from use in turbines and pumps in the nuclear industry. This approach would be an alternative to the established solution of incineration when this is unsuitable due to issues of either cost, levels of radioactive contamination, and/or local UK stakeholder objection. This process, by virtue of its low energy requirements, is also less environmentally damaging (reduced carbon footprint) than the energy intensive coincineration of these contaminated oils with fuel-oil.

Treatment is achieved by creating an oil/water emulsion, contacting this with Nyex® through fluidization where adsorption of the oil onto the Nyex® surface is achieved. After adsorption the adsorbent settles to create a bed through which a current is passed to oxidise the organics and regenerate the adsorbent. The bed of regenerated Nyex® adsorbent is then re-fluidised for further adsorption, the cycle being repeated until the oil has been removed (Fig 1). The adsorbed oil is hence electrochemically destroyed with the radioactive contamination partitioned between the aqueous phase and the Nyex® adsorbent. These secondary wastes can then be conditioned using established technology and consigned to existing regulator authorised disposal routes. It should be noted that the supernatant can be reused to create the next batch of emulsion until the radioactive burden (dissolved radioactivity-suspended radioactive particulate) reaches a concentration that prompts disposal.

The removal of oil has been followed by TOC analysis (Fig 2) over a number of adsorption/regeneration cycles, showing oil removals to low levels, even when additional oil is added. Solid phase TOC and thermogravimetric analysis will be used to follow the oxidative destruction of the adsorbed oil. Analysis of the supernatant aqueous layer after adsorption by TOC indicates that loadings on the adsorbent as high as 60% w/w are achievable. This process appears to have the potential to treat a problematic waste in the nuclear industry, producing a secondary aqueous waste stream that is amenable to treatment using existing technology. It destroys the oil releasing the radioactivity into the aqueous phase.

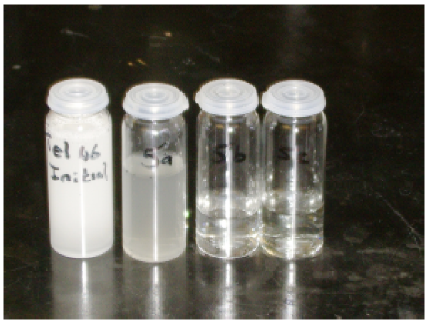

Fig 1 - Change in the appearance of a 1% Tellus 46 emulsion after 4 adsorption / regeneration cycles.

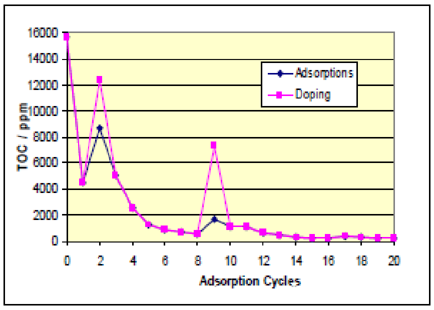

Fig 2 - Adsorption cycles for 5% w/v Tellus 46 emulsion in tap water with additional oil emulsions added after 2 and 9 cycle

EXTRACTION OF TECHNETIUM(VII) AND RHENIUM(VII) BY THE NEW REAGENT, 2-(IMINO)BIS(N,N-DIALKYLACETAMIDE) (IDAA)

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2,2’-(Methylimino)bis(*N,N*-dioctylacetamide) (MIDOA) and 2,2’-(Imino)bis(*N,N*-dioctylacetamide) (IDOA), as the 2,2’-(Imino)bis(*N,N*-dialkylacetamide) derivatives(IDAA), was reported for a new extractant. MIDOA, whose structural formulae is CH3N-(CH2CON(C8H17)2)2, has a nitrogen donor atom in the ether position between two amide groups and may shows the tridentate chelation. MIDOA, having four *n*-octyl groups, can be dissolved well in *n*-dodecane and used readily for the extractant. Not only Tc(VII) but also Cr(VI), Re(VII), Mo(VI), W(VI), and Pd(II) are extracted by MIDOA and IDOA from the diluted HNO3 and *D*(Pu) shows the maximum value at 3M HNO3. MIDOA has somewhat higher *D*(Tc) than IDOA and may show the strong bond with metals. The extraction capacity (LOC) of Re(VII), which is used as the substitution of Tc(VII), is more than 37 mM, and the third phase was hardly seen during extraction. The water-soluble IDAA can be prepared by the attachment of short alkyl chain with N atoms in the amide groups, and MIDEA and IDEA, having four ethyl groups, are dissolved in water. These reagents may be used for the reverse-extraction of Tc. In this presentation, we discuss about the results of extraction and reverse-extraction of Tc (Re), stability of reagents and structural study on calculation.

4-PS1 13681

RADIOCHEMICAL EDUCATION AND TRAINING IN CHINA

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Nuclear and radiochemistry research, education and training in China can be traced to 1935, when a few of old generation of radiochemists were back to China after they got trained in the west. It reached the top in the fifties and sixties, last century, the so-called golden season for radiochemistry. However, it entered the declining stage in the 1980s and 1990s, the same as other countries in the world. Gladly, radiochemistry is at renaissance after the beginning of the new millennium. In China it is called the second Spring for nuclear science and radiochemistry. A strong impetus for radiochemistry is attributed to the rapid development of nuclear energy in China. In average, two nuclear power facilities per year will be installed since now on. Nowadays there are 25 schools (or colleges) of nuclear science and technology (or engineering) in Chinese universities, of which 13 have nuclear and radiochemistry education and training with about 300 undergraduate students per year. The number of master and doctorate students in radiochemical field is about 50 annually. Several universities and institutes have research reactors, accelerators, neutron generators and other nuclear facilities used for radiochemical education and training. An exciting fact is that some big scientific platforms have been, are being or will be constructed, e.g. the Chinese Advanced Research Reactor, Shanghai Advanced Light Source, Chinese Spallation Neutron Source and other big nuclear facilities, which are providing or will provide radiochemists with advanced nuclear arsenal. However, a quite number of problems in Chinese radiochemical educations still exist, among which the biggest one is shortage of bright young radiochemists in China. In the meantime, experienced radiochemical teachers are urgently needed. Some radiochemical laboratories in Chinese universities are outdated and ill-equipped. Some measures and strategies for pushing radiochemistry in China will be proposed in this text as well.

5-TS8-1 13793

EVALUATION FOR Po-210 INTAKE THROUGH FISH AND SHELLFISH CONSUMPTION BY JAPANESE

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Fish and shellfish are the main foodstuffs for Japanese and a considerable amount is consumed customary as raw fish. Polonium-210 concentrations in marine organisms are known to be relatively high that would cause a significant internal dose for Japanese through diet.

To evaluate Po-210 intake from fish and shellfish and to estimate resulting dose for Japanese, Po-210 concentrations in fish and shellfish are determined by alpha spectroscopy following wet decomposition of samples.

Shellfish showed higher concentrations than fish probably due to higher concentrations of Po-210 in internal organs. No separation of internal organ was carried out for shellfish because whole body of the shellfish is usually consumed. A muscle part of fish was analyzed basically considering an eating habit in Japan. Po-210 concentrations in major fish species are distributed widely; therefore Po-210 intake varies depending on fish consumption of each species and its Po-210 concentration. Small fish analyzed including its internal organ showed Po-210 concentration comparable to shellfish, probably suggesting high Po-210 content of internal organs of fish. Fish species and their amounts consumed over Japan differ greatly indicating intake of Po-210 also differs and is characterized locally.

5-S8-2 17205

REACTION OF PLUTONIUM(VI) WITH MANGANESE-SUBSTITUTED GOETHITE

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The proper handling and storage of high-level radioactive waste in underground repositories requires basic knowledge of the molecular interactions controlling the transport and migration of actinides in the environment. Investigations of the interfacial reactions at the boundary between aqueous radionuclide solutions and minerals are especially important to further current knowledge of these processes and to accurately predict the fate of radionuclides as they migrate through the geosphere. Previous work on the sorption of Pu(VI) onto goethite (α-$Fe^{III}OOH$), a common component in soils, has shown that reduction of plutonium does not occur on this iron oxide surface[1]. However, previous and on-going work with pure manganese mineral phases have shown that these minerals can reduce plutonium from Pu(VI) to Pu(IV) upon contact[2], although the exact plutonium reduction mechanism is still unclear. In nature, manganese is often only found as a minor component in soils and is usually associated with other more prevalent mineral phases.

We explore the mechanism of Pu reduction as well as the sorption environment of plutonium on the surface of environmentally relevant minerals. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, an atom specific technique, allows us to measure the in-situ oxidation state and coordination environment of the absorbing atom. This technique, along with other methods, is used to measure the reaction of Pu(VI) with manganese-substituted goethite ($[Fe^{III}_{1-x}Mn^{III}_{x}]OOH$) at varying percent substitutions of manganese. Results from the measured plutonium sorption isotherms, oxidation state analysis, and coordination environment are discussed.

[1] D. A. Shaughnessy, H. Nitsche, C. H. Booth, D. K. Shuh, G. A. Waychunas, R. E. Wilson, H. Gill, K. J. Cantrell, and R. J. Serne. Molecular Interfacial Reactions between Pu(VI) and Manganese Oxide Minerals Manganite and Hausmannite. Environmental Science & Technology, 37:3367, 2003.
[2] Richard E. Wilson. Reactions of Plutonium(VI) with the Iron Oxide Goethite. PhD thesis, University of California, Berkeley, 2005.

The research was performed under appointment of the Office of Civilian Radioactive Waste Management Graduate Fellowship Program administered by Oak Ridge Institute for Science and Education under a contract between the U.S. Department of Energy (DOE) and Oak Ridge Associated Universities, and is also supported by the DOE under Contract No. DE-AC02-05CH11231. X-ray absorption data were collected at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the DOE/OBES.

OBSERVATION OF ^{228}Ra/^{226}Ra ACTIVITY RATIO, AND CONCENTRATIONS OF ^{226}Ra AND ^{228}Ra OF SURFACE SEAWATERS IN THE PACIFIC SIDE OF JAPAN

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Recently, it is one of the research items that the investigation of the trace elements supply process from coastal zone is important in the GEOTRACES plan of the Asian district. The biological production by the phytoplankton is greatly influenced by the trace element, including Fe, Co, Si and Zn, supplied from the coastal zone. It is important to know the process that the trace element transports to the surface and the quantity supplied to consider these influences. The observation of environmental radioactivity in seawater supplied from coastal zone is useful also for the decision of the species composition and the parameter of biosphere.

We mainly deals with an observation of ^{228}Ra/^{226}Ra activity ratios in the surface seawaters on the Pacific Ocean side of the central Japan at the following 4 sampling sites: (1) five ports in Izu-Oshima locating on open sea slightly apart from Japanese Islands, (2) Ajiro Port, Atami, in Sagami Bay on the Pacific Ocean, (3) Umidzuri Park, Yokohama, at the inner part of Tokyo Bay, semi-closed estuaries and (4) Kuroshio.

The Ra isotopes in the surface seawaters were collected almost for two or three times a year on Mn impregnated acrylic fiber at the ports in Izu-Oshima from 2003 to 2006, and once a month at Atami from Spring from 2005 to 2006, and for once a month at Umidzuri Park in period from 2004 to 2006. The ^{228}Ra/^{226}Ra activity ratio in the surface seawaters ranged from 0.2 to 0.7 for Izu-Oshima, from 0.2 to 0.7 for Sagami Bay and from 0.6 to 0.8 for Tokyo Bay. The ^{228}Ra/^{226}Ra activity ratio showed low value from beginning of winter to beginning of spring. The activity ratios in the surface seawaters of Izu-Oshima and Ajiro port of the vicinity of Sagami Bay were clearly low in winter and spring, and high in summer and autumn, while Umizuri Park of Tokyo Bay less clearly showed variation pattern than the other sampling sites. The range of variation in the surface seawaters between winter and autumn in 2005 was 3 times for Atami and 1.2 times for Umiduri Park. The reasons for variation pattern of the ^{228}Ra/^{226}Ra and range of variation are discussed.

FIRST RESULTS ON ^{236}U LEVEL IN SOILS FROM GLOBAL FALLOUT-APPLICATION FOR HIROSHIMA BLACK-RAIN ISSUE

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With recent developments of analytical instruments and measurement techniques able to detect ultralow amount of ^{236}U ($T_{1/2}$=2.342×10^7 y, α-decay) in the environment. U-236 is being recognized as a potential tracer not only for monitoring of uranium contamination release from nuclear cycle, but also for geochemical dynamics studies.

For accurate determination of ^{236}U in the environment at low level, the ^{236}U input from global fallout has to be considered. However, information on ^{236}U background has not been clearly defined. In current study, ^{236}U along with $^{239+240}$Pu and ^{137}Cs, were measured to estimate their isotope ratio, concentration and inventory in soil samples from forest in Ishikawa, Japan. This area has not been affected by local or regional ^{236}U releases from nuclear facilities or the Chernobyl accident. The activity of ^{137}Cs, $^{239+240}$Pu, ^{238}U and ^{236}U/^{238}U atom ratio in the soil (0-10, 0-20 and 0-30 cm) were measured with γ-ray and α-spectrometries and accelerator mass spectrometry (AMS). The ^{236}U/^{238}U isotopic ratio and ^{236}U concentration ranged from 1.85×10^{-8} to 1.09×10^{-7} and 8.92×10^{8} to 3.76×10^{9} atoms/g dry soil, respectively. The average ^{236}U/^{239}+^{240}Pu ratio (atoms/Bq) was $(1.56\pm0.10)\times10^{11}$. That translates into the ^{236}U/^{239}Pu atom ratio of 0.235 using the global fallout ratio for ^{240}Pu/^{239}Pu of 0.176. This is within the range of 0.05 - 0.5 reported for the locations with high ^{239}Pu and low ^{238}U soil concentrations (Ketterer et al. 2007). No significant correlation was found between ^{236}U and ^{137}Cs concentrations in measured soils as opposite to $^{239+240}$Pu.

Our results indicate that surface soil has been contaminated with ^{236}U from globalfallout of 10^8 – 10^9 atoms/g (10^{13} atoms/m^2 in soil from this area). The total surface soil deposition of ^{236}U due to global fallout was estimated as ca. 900 kg. The study was undertaken to characterize the Black Rain area of Hiroshima atomic bomb. The distributions of ^{236}U, $^{239+240}$Pu and ^{137}Cs isotopes were measured in more than 60 surface soil samples from Hiroshima. The results of this study will be presented and discussed in the presentation.

Ketterer ME, Groves AD, Strick BJ, Goldschmidt Conference Abstracts, Geochim. Cosmochim. Acta 2007:71;A480.

5-S8-5 20609

DETERMINATION OF PLUTONIUM, URANIUM, STRONTIUM AND AMERICIUM/CURIUM ISOTOPES IN ENVIRONMENTAL SAMPLES WITH ANION EXCHANGE, UTEVA, SR AND DGA RESIN

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This study presents a rapid and quantitative radiochemical separation method for the Pu, U, Sr and Am/Cm isotopes with an anion exchange resin, UTEVA resin, Sr resin and DGA resin sequentially. After the sample solution adjusted with 8M HNO_3 was passed through columns (an anion exchange column connected with an UTEVA column, a Sr Spec column and DGA column), the Pu, U, Sr and Am/Cm isotopes were sequentially adsorbed on the columns. Pu isotopes were purified from other nuclides through the anion exchange column, and the uranium isotopes were separated from other nuclides through the UTEVA column. Also, ^{90}Sr was separated from other hindrance elements with the Sr Spec column. Finally, Am/Cm fractions were purified with the DGA resin. For the purified Pu, U and Am/Cm isotopes, microcoprecipitation or electrodeposition method was used for an alpha source preparation. The activity concentrations and activity ratios for the Pu isotopes were measured by radiation counting methods such as an alpha spectrometry and a liquid scintillation counting. The U and Am/Cm isotopes were measured by an alpha spectrometry. Strontium-90 was measured by a low level liquid scintillation counter. The radiochemical procedure of Pu, U and Am nuclides investigated in this study has been validated by application to IAEA Reference soils.

5-S8-6 16700

PO-210 IN WATER AND FISH FROM CENTRAL ASIA URANIUM MINING AND TAILING SITES

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In most countries, uranium mining is considered the most hazardous step of nuclear materials production, both in terms of radiation doses and in the number of people affected. Key problems have been associated with the transport of uranium and its daughters in aquatic and terrestrial ecosystems, where radionuclides are transferred from air, water, and soils into plants, animals and finally to man. Special attention is paid to the most hazardous decay products of uranium; Pb-210 and Po-210 and Ra-226 in soils, waters and plants. A certain fraction of uranium and decay products will be present as radioactive particles and the transfer to man occurs via inhalation from resuspension as well as dietary intake. It is assumed that 40 % of the world reserves of uranium are situated in Kazakhstan, Kyrgyzstan and Tajikistan. Following the cold war, extensive uranium mining and production took place at numerous sites in the former Soviet Union.

Po-210 in water and fish has been determined as part of a Joint project between Norway, Kazakhstan, Kyrgyzstan and Tajikistan. The project aims to assess long term consequences of TENORM waste, evaluate the need for alternative countermeasures and strengthen the scientific competence of the national authorities in the Central Asian region. Emphasis is put on the radioactive contamination associated with uranium mining and milling and the project aims to assess the activity and distribution of TENORM within the ecosystems. The objective of this specific work is to provide first hand information on the concentration of the naturally occurring radioactive isotope ^{210}Po, based on speciation analysis of water and by analysis of different fish organs from an area of former uranium mining activity in Tajikistan. The average concentration of ^{210}Po in liver of *C. auratus* from Taboshar mining area in Tajikistan is 3648 ± 860 Bq kg-1 ww. The activity concentration of ^{210}Po in muscle of *C. auratus* from study site, compared to similar organs of *S. lucioperca* in Kyrgyzstan and Kazakhstan mining areas, increased with a factor of ~250 and ~500, respectively. Further, the activity concentration of ^{210}Po in liver of *C. auratus* increased with a factor of ~400 compared to the activity concentration in liver of *S. lucioperca* from Kazakhstan. The activity concentration of ^{210}Po in liver showed a significant linear relation to δ15N in *C. auratus*, indicating a biomagnificating property of ^{210}Po.

5-S8-7 17573

RAPID SEPARATION AND EXTRACTION OF RADIOACTIVE ANALYTES ONTO FILTERS AND MEMBRANES

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Current radiochemical analysis techniques require time consuming wet separation methods to prepare samples for analysis by alpha spectrometry. This presentation presents a method to combine radiochemical sample preparation and analyte separation to provide a rapid sample preparation approach. Extractive ligands are prepared in a polymer matrix. This system can be immobilized on a surface, on a filter, or prepared as a thin membrane. Filters allow rapid sample uptake due to the movement of the analyte through the filter material. The thin membrane approach allows the analyte to be prepared and detected on either side of the membrane. These approaches offer fast uptake kinetics, high material loading, and good selectivity. These systems have been demonstrated for the rapid extraction (1-2 hours) of plutonium and americium from solution and their subsequent analysis by alpha spectrometry, with no additional sample preparation required, thus eliminating extensive wet chemical processes that would otherwise be necessary. We have evaluated the extraction efficiency that can be obtained and have shown that these systems can provide for alpha spectrometry peak widths near what can be obtained using traditional techniques such as electroplating. We have also demonstrated PLFs for the selective extraction of plutonium or americium from urine as a potential bioassay technique. (LAUR-09-4421).

RADIOACTIVITY IN THE ARCTIC ENVIRONMENT

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Previous AMAP assessments of radioactivity in the Arctic have highlighted that the Arctic terrestrial environments is more vulnerable to radioactive contamination than many other parts of the world. Moreover, they have shown that past sources such as fallout from nuclear testing in the 1950s and 1960s and the 1986 accident at the Chernobyl nuclear power plant still contribute to human exposure. The 2002 assessment also highlighted continued releases to the marine environment from European reprocessing of nuclear waste and the risks associated with handling spent nuclear fuel and radioactive waste in northwest Russia. The current assessment (2009) provides an update of sources of radioactivity to the Arctic environment, including the results of efforts to reduce the risks associated with waste handling and decommissioning of old nuclear powered equipment. It also discusses changes in the range of actual and potential sources and highlights that non-nuclear industrial activities may increase the release of naturally occurring radioactive substances to the environment. While previous assessments have mainly addressed the risks of radioactivity related to human health, this assessment also addresses the impacts on non human biota due to the vulnerability of Arctic ecosystems. In addition, it includes a discussion of how climate change may affect radioactive contamination in the environment.

INCREASING RADIOANALYTICAL CAPACITY – PREPARING YOUR LAB

Jack Bennett

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As the state of the nation's ability to respond to a radiological event is examined, it has become apparent that both capacity and capability are lacking. Department of Homeland Security National Planning Scenario #11 is designed to address the planning activities for the response to an attack using radiological dispersal devices. The scenario details that the cleanup activity will take several years, and that there will be between 360,000 and 1,000,000 environmental samples in the first year. Based on existing capacity and capabilities it would take four to six years to analyze the samples generated at the lower end of the sample range.

The Environmental Protection Agency (EPA) has been given responsibility for the remediation activities following a radiological event, and has awarded cooperative agreements to several laboratories to start the process of developing capacity and capabilities. The Connecticut Department of Public Health Laboratory (DPHL) was awarded one of the cooperative agreements and has started activities to further those goals by investigating and implementing more rapid methods for radiochemical analysis. The DPHL already served as the primacy radiochemistry laboratory for several New England states and thus had a solid foundation to build upon. This presentation will discuss activities that the DPHL has taken to fulfill the cooperative agreement, share items to consider when implementing radiological emergency response activities in a laboratory and also share some lessons learned.

5-S8-10 17188

ISOLATION, CLONING AND CHARACTERIZATION OF SILVER-110m BINDING PROTEIN (HEMOCYANIN-TPb) FROM LIVER OF SQUID

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National Research Institute of Fisheries Science of Fisheries Research Agency has monitored artificial radionuclides in marine organisms and confirmed the safety of fishery products collected around Japan since 1957. In this program, silver-108m is still detected only from liver (or midgut gland) of some mollusks in recent studies. Although some metalloproteins like metalothionein, ferritin and hemocyanin are known to be involved in the accumulation of these radionuclides in mollusks [1], the specificity and mechanisms of accumulation are not fully characterized.

In this study, we show isolation, cloning and characterization of a silver binding protein (Hemocyanin-TPb) from the liver of squid using silver-110m.

Liver sample of flying squid (*Todarodes pacifics*) was homogenized in buffer containing 1.2 kBq/mL of Ag-110m tracer at final concentration. After centrifugation, 4.2, 78 and 17% of added Ag-110m was distributed to lipid, soluble protein and insoluble protein fraction, respectively. A silver binding protein was purified by gel filtration and ion exchange column chromatography monitoring radioactivity of Ag-110m in the fractions. The purity was examined with SDS-PAGE, and the 67 kDa band was substituted to peptide sequencing analysis (Fig. 1). Obtained partial sequences of the squid silver binding protein had a homology with hemocyanin of a crayfish (*Pacifastacus leniusculus*) by BLAST search. We cloned 10,071 bp of cDNA encoding a hemocyanin (3,357 aa) from flying squid and named it Hemocyanin-TPb. There were eight function units in Hemocyanin-TPb as well as other molluscan hemocyanins. Because the size of Hemocyanin-TPb was too large to be expressed in *E. coli* cells, we constructed expression vectors containing one or more function units in MCS. Characterization of recombinant Hemocyanin-TPb will be discussed in the presentation.

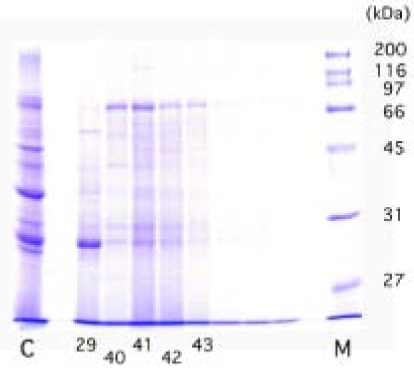

Fig. 1. SDS-PAGE of purified silver binding protein in *Todarodes pacificus*. C: crude sample, 29-40: fraction number of sample, M: Marker.

[1] Bioaccumulation and toxicity of silver compounds, Ratte H. T., *Environ. Toxicol. Chem.*, **18:**89-108 (1999)

5-S8-11 18789

AUTOMATED RADIONUCLIDE SEPARATION SYSTEM FOR FIELD LABORATORY AND/OR FIXED LABORATORY USE

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There exists a need to quickly measure both alpha and beta emitting nuclides in a field environment, especially for radiological emergencies where such data is critical in making rapid health and safety decisions. Measurement of many nuclides requires chemical separation before accurate counting can be performed; a difficult task in a field environment. A field deployable automated radionuclide separation system is being designed to perform a sequential separation of key radionuclides in under one hour. Preliminary data indicates that this design goal is attainable. A prototype system is currently being constructed for testing and validation by the US Air Force.

5-S8-12 17423

STRUCTURE OF PLUTONIUM COLLOID WHEN ASSOCIATED WITH DIFFERENT MINERALS

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Recent field studies have shown subsurface transport of Pu over Km length scales, where the Pu is associated with colloidal particles and not the dissolved fraction (e.g. [1], [2]). Yet despite these observations and a body of experimental and modeling studies, a comprehensive understanding of the mechanism of colloid-facilitated transport of Pu remains elusive. For example, very little is known about the geochemical and biochemical mechanisms controlling Pu-colloid formation and association. This lack of understanding limits our ability to model and predict transport.

In this study, we evaluated the surface structure of Pu with several minerals. Pu colloids were formed in oversaturated conditions ($[Pu(IV)] = 10^{-6}M$). Pu colloids were then sorbed to several minerals and its structure examined. Results using High-Resolution Transmission Electron Microscopy (TEM) show that when Pu colloids were formed in solution the expected fcc fluorite-type structure of PuO_2 was observed. When the Pu colloids were sorbed on the surface of silica the fcc fluorite-type structure of PuO_2 was also observed. However, when Pu colloids were sorbed to goethite {100} surfaces, the Pu colloid structure matched bcc Pu_4O_7 rather than fcc PuO_2. This structural distortion appears to be related to the lattice match that results in a strong parallel correlation between the goethite {021} crystal planes and the Pu_4O_7 {114} crystal planes. We speculate that the structural distortion of the Pu colloids results from a stronger interaction between Pu colloids and goethite surfaces, relative to silica surfaces and that this structural distortion will affect the solubility of Pu colloids.

[1] Kersting et al., *Nature.* **1999**, *397*, 56-59.
[2] Novikov et al., *Science.* **2006**, *314*, 638-641.

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SEQUENTIAL ANION EXCHANGE SEPARATION OF TRACE URANIUM, THORIUM, LEAD AND LANTHANIDES IN ENVIRONMENTAL SAMPLES

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Abundance and isotopic ratios of trace uranium, thorium, lead and lanthanides in a sample play a key role to investigate features of environmental samples. From the ratios of these key elements, information on origin and history of the sample can be obtained. Much amount of co-existing elements affect accuracy of isotopic ratio of uranium measured by ICP-MS. For examples, alkaline metals affect the mass bias of the instrument[1], and polyatomic ions of tungsten overlap with the uranium isotopes (e.g. $^{186}W^{16}O_3$ for ^{234}U, $^{186}W^{16}O_3H$ for ^{235}U)[2]. The key elements should be separated from the coexisting elements and these interfering elements in a sample to analyze accurately the abundance and isotopic ratios of the key elements.

In this work, sequential anion-exchange separation techniques of trace U, Th, Pb and lanthanides in environmental (geological) samples were developed. Nano grams (10^{-9} g) of U, Th, Pb and lanthanides in a geological reference rock were sequentially separated with a single anion-exchange column. Mixture of acetic acid, HCl and HNO_3 were used as the eluents for this separation. The recovery of these key elements was more than 95%, and there was no fractionation among the recoveries of each lanthanide element. Alkaline metals, alkaline earth metals and Fe were effectively eliminated from the key elements. By using this technique, it is possible to simplify the complicated traditional processes without any special ligands, columns and equipments. Ion exchange separation of W from U in environmental samples with the mixture of HCl and HF will be also mentioned.

[1] Effect of alkali metals on the accuracy of isotope ratio measurement of uranium by ICP-MS. M.Magara et al., *J. Anal. At. Spectrom.*, 17, 1157 (2002).

[2] Assessment of plutonium measurement in the femtogram range by ICP-MS; correction from interfering polyatomic species. F.Pointurier et al., *J. Anal. At. Spectrom.*, 23, 94 (2008).

5-S8-14 16224

ACCELERATOR MASS SPECTROMETRIC MEASUREMENTS OF PLUTONIUM ISOTOPES IN SOIL SAMPLES COLLECTED FROM ENEWETAK ATOLL IN THE NORTHERN MARSHALL ISLANDS

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Enewetak Atoll is a former U.S. atmospheric nuclear weapons test site located in the northern Marshall Islands. The atoll consists of 46 small islets occupying about 7.6 km^2, surrounding a lagoon about 80-km in circumference. A total 43 atmospheric nuclear tests were conducted in the near-surface marine and terrestrial environment of Enewetak Atoll between 1948 and 1958. The test program led to localized contamination of islands and the atoll lagoon by close-in fallout deposition containing a range of fission and activation products as well as unfissioned nuclear fuel. We have recently characterized residual levels of plutonium contamination on land and parts of the lagoon using Accelerator Mass Spectrometry (AMS). AMS has a detection sensitivity around 5×10^5 atoms (e.g., ~0.5 µBq ^{239}Pu) and provides a basis for studying plutonium contamination in the environment using characteristic isotope ratios (e.g., ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu, ^{242}Pu/^{239}Pu, and ^{244}Pu/^{239}Pu atom ratios) generated from specific types of nuclear events. These measurements demonstrate that plutonium signatures in aged fallout on Enewetak are readily distinguishable from those measured in global fallout deposition, and show a distinct geographical distribution with higher levels (> 1 ng g^{-1}, dry soil) and isotope ratios (^{240}Pu/^{239}Pu > 0.3) occurring in surface soils collected from the more northern reaches of the atoll. Plutonium isotopic signatures from separate nuclear test events also appear to be more easily recognizable in soils than previously envisaged and are best represented on a mixing line between low-yield and high-yield test events. A number of soils collected from the northern islands on the atoll contain plutonium isotopic abundances that are indistinguishable from that previously measured in prompt fallout debris generated from the 1952 Mike thermonuclear test. The plutonium isotopic content of soil samples on Runit Island is very different. These soils are known to contain dispersed nuclear fuel fragments from safety and/or low-yield tests. Overall, this study yields new information on the isotopic composition of residual plutonium contamination of coral soils on Enewetak Atoll, and gives a good demonstration of the utility of using AMS plutonium isotope measurements for source-term characterization.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory in part under Contract W-7405-Eng-48 and in part under Contract DE-AC52-07NA27344.

PERSPECTIVE ON JAPANESE FUEL CYCLE AND EXPECTATION TO TECHNICAL ADVANCEMENTS

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The Japanese prime minister recently announced a new mid-term target for GHG reduction, which includes a 15 percent reduction from the 2005 level. In order to achieve this aggressive goal, nuclear power generation is expected to supply more than 40% of the total Japanese electricity consumption by 2020. This means extensive modification of the operation of nuclear power plants, as well as establishment of a steady fuel cycle is required. In Japan, the initial commercial MOX fuel loading to LWR will start soon, as will the commissioning of the Rokkasho Reprocessing Plant. Through these two key steps, Japan will enter the commercial stage of the closed fuel cycle, and this will have an extensive significance for accomplishing the Japanese future nuclear power utilization goal of 40%. In this paper, the latest status of these two significant fuel cycle activities will be briefly described. In this context, a preliminary investigation was performed to clarify the design operating conditions and requirements for the follow-on reprocessing plant which will be expected after the life-end of the Rokkasho Reprocessing Plant. This investigation focused on the future period from 2050 to 2100, which is a transitional period from LWR to FBR giving particular consideration to the design of the next reprocessing plant. This result indicates that more strategic and realistic planning as well as strong research and development will be needed. The results of this investigation, as well as the progress of the Japanese FBR fuel cycle development will be described.

From last year through early this year, the Japan Atomic Energy Commission reviewed the progress of Partitioning and Transmutation Development in Japan. In this review, the meaning of P&T development, anticipated effect of the transmutation, as well as the technological progress were thoroughly studied. In this review, both (1) Fast Breeder Reactor System with homogeneous MA loading, and (2) Accelerator Driven Subcritical System (ADS) were assessed. As a result, technical issues to be solved and other requirements for the future development were cleared up and a new direction was shown. The results of this study will be described in this paper.

6-S4-2 17607

CURRENT STATUS AND PERSPECTIVE ON FAST REACTOR FUEL CYCLE TECHNOLOGY DEVELOPMENT PROJECT IN JAPAN

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Japan Atomic Energy Commission determined the basic policy on R&D of FR cycle technologies over the next decade on December 26, 2006. In this determination, it was described that the concerned parties (JAEA, MEXT, METI, electric utilities and manufacturers) would corporate to promote R&D regarding the select concept and produce by 2015 the conceptual designs of commercial and demonstration FR cycle facilities with R&D programs to be realized them.

Since discussions starting around 2010 on the second nuclear fuel cycle reprocessing plant are set to cover a strategy of transition from the light-water reactor (LWR) cycle to the FR cycle, the FR Cycle Commercialization R&D program shall aim to provide scientific and technological knowledge contributing to this discussion.

In this context, JAEA have been launched the "Fast Reactor Fuel Cycle Technology Development (FaCT)" Project since 2006, to take over Feasibility Study on commercialized FR cycle in Japan. The main concept in the FaCT Project, which should be developed principally for most promising for commercialization, is the combination of the sodium-cooled fast reactor with oxide fuel, the advanced aqueous reprocessing and simplified pelletizing fuel fabrication. In Phase I of FaCT Project for 5 years (JFY2006-JFY2010), it is important to determine innovative technologies to be adopted and to establish commercial concepts that excel in economy, maintainability and repairability.

In this paper, the following 3 issues will be briefly presented:

Medium- to long-term plan around and beyond including transition from LWR cycle to FR cycle

In the first issue, the current status of the preliminary study and examination for the transition of LWR cycle to FR cycle in cooperation with the concerned parties will be introduced, which will be submitted for intensive discussion on the subsequent reprocessing plant to RRP which will be started in Japan Atomic Energy Commission around 2010.

Near–term plan around 2015 in FaCT Project

Design study and R&D of innovative technologies are now in progress aiming at adopting of innovative technologies by judging of their applicability in JFY2010, and presenting the conceptual designs of commercial and demonstration facilities in JFY2015 in FaCT Project. The interim report in Phase I of FaCT Project has been compiled, so the content of this report will be presented briefly in the second issue.

Main issues to be studied in advanced fuel cycle in Japan

TRU recycling in Advanced Fuel Cycle in this last issue is addressed. It is also mentioned that in revolutionary type R&D, international collaboration plays an important role in development of fast reactor cycle technologies, as its development actually needs a long-term efforts and large resources.

APPROACHES TO MANAGING MINOR ACTINIDES IN ADVANCED NUCLEAR FUEL CYCLES

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The basic framework for uranium and plutonium separation and recycle as it is known today (the PUREX process) was established more than 50 years ago. After 50 years, minor adjustments are still being made to improve the performance of this workhorse process. However, future adaptations of the basic closed nuclear fuel cycle will almost certainly take on a new approach, emphasizing not just Pu recycling, but a more complete waste management plan. The first priority of advanced nuclear fuel cycles will be to accomplish Pu recycle without increasing weapons proliferation risks. The second most important objective of advanced nuclear fuel cycles will by minimizing the potential deleterious effects of the minor actinides, principally Am and Np. Neptunium may ultimately prove to have value as source material for the production of 238Pu for Radionuclide Thermal Generators (RTGs), hence recycle of Np for transmutation could be pursued. In contrast, Am is produced in far greater abundance than is demanded by any presently recognized commercial application (primarily smoke detectors). The objective of minimizing the long-term radiotoxicity of the byproducts of fission probably will be best served by the purposeful transmutation of Am in advanced fast neutron spectrum reactors. In almost any scenario for the transmutation of Am, its separation from fission product lanthanides will be needed. In this presentation, selected features of various separation options for minor actinide management will be discussed, emphasizing the various approaches that are currently under investigation globally.

6-S4-4 22182

EXTRACTION SEPARATION OF TRIVALENT MINOR ACTINIDES FROM LANTHANIDES WITH HEXADENTATE NITROGEN-DONOR LIGANDS, TPEN AND ITS DERIVATIVES

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The extraction separation of MA (minor actinides) and Ln (lanthanides) with podand-type hexadentate ligands, TPEN (*N,N,N',N'*- tetrakis(2-pyridylmethyl)ethylenediamine) and its derivatives, was studied for the recovery of MA from HLLW generated in spent nuclear fuel reprocessing plants. The extraction behavior of Am(III) (MA) and Eu(III) (Ln) with TPEN diluted with organic solvents, such as nitrobenzene and 1-octanol, was tested. TPEN showed good Am(III) selectivity, namely $SF_{Am/Ln} \sim 100$, in the pH range over 5. However, from the viewpoint of practical application, both high extractability and high Am(III) selectivity is required in the pH range below 4. The hydrophobicity of TPEN should be enhanced to decrease the dissolution of TPEN to water.

In this study, long alkyl chains were introduced to four pyridine rings of TPEN and the effect of the introduction of alkyl groups on the separation of Am(III) and Eu(III) was tested. Both the extractability and the Am(III) selectivity were increased with increasing the length of alkyl groups in the acidic solution below pH4. TOPEN (*N,N,N',N'*-tetrakis((5-octyloxypyridin-2-yl)methyl)ethylenediamine) showed excellent separation performance of Am and Eu. The $SF_{Am/Eu}$ value of about 50 was obtained at pH3. When a hydrophobic carboxylic acid was added as a synergist, the extractability of TPEN derivative connecting long alkyl groups was further improved. Then, the $SF_{Am/Eu}$ was increased to more than 200 at pH3.

This research was supported financially by MEXT (Ministry of Education, Culture, Sports, Science and Technology).

Am/Eu CHROMATOGRAPHIC SEPARATION WITH NEW SOLID EXTRACTANTS BASED ON C5-BTBP

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The 6,6'-bis-(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2']bipyridinyl (C5-BTBP) extractant was recently demonstrated to separate efficiently minor actinides (MAn) from the reprocessing waste using liquid–liquid extraction. High separation factors between MAn and lanthanides could be achieved in one stage [1].

At the Czech Technical University in Prague (CTU), Centre for Radiochemistry and Radiation Chemistry and the Department of Nuclear Chemistry, the studies directed towards proposal of a chromatographic process for the partitioning of minor actinides from high active liquid waste are carried on [2]. For the second stage of this process – selective separation of the actinides from the lanthanides – solid extractants (SEXs) with C5-BTBP have been considered.

For the initial study, a novel C5BTBP–PAN solid phase extractant was prepared in-house by incorporating the solid powdered C5-BTBP extractant into the binding matrix of modified polyacrylonitrile (PAN). Acceptable extraction properties of this material were reached only after dissolving the solid C5-BTBP in a suitable diluent. The study of the influence of different diluents revealed that the most prospective systems are the solid extractants prepared by impregnation of neat PAN beads with solutions of C5-BTBP dissolved in tetrachloroethane, nitrobenzene, or cyclohexanone. With these materials, high separation factors SF ~ 100) were achieved. However, the kinetics was rather slow (in 3 hours the uptake of americium attained ~65 % of its equilibrium value). The dynamic column experiments with PAN C5BTBP[tetrachloroethane] and PAN–C5BTBP[nitrobenzene] showed that the behaviour of C5 BTBPbased solid extractants in packed beds does not exactly follow the behaviour of this material in batch experiments; insufficient mutual separation of Am and Eu was reached.

In the next phase another solid extractant – E5–C5BTBP[nitrobenzene] – was prepared by impregnating the Synachrom E5 (Lachema, Czech Republic) support with the solution of C5-BTBP in nitrobenzene. In a column experiment with this solid extractant, europium was almost quantitatively (> 98.6 %) washed out of the column with 1M HNO3 while americium was retained in the column (less than 0.3 % washed with the Eu fraction). The sorbed americium could be efficiently eluted with 0.5 M glycolic acid with pH 4, the americium fraction contained less than 1.4 % of the original amount of europium. These results are very encouraging, the system was proposed for further more detailed study.

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6-S4-6 15533

CHROMATOGRAPHIC SEPARATION OF Am AND Cm

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Americium (Am) and curium (Cm) are trivalent elements that are produced during irradiation of nuclear fuels and nuclear targets, and that have very similar chemistries. This similarity in the chemistries makes their separation from each other challenging. Reports have appeared in the literature on Am/Cm separation using tertiary pyridine type resin with acid/alcohol mixed solvent1. However, because this chromatographic material is not commercially available, this procedure requires fabrication of the resin in house. A new method using a commercially available extraction chromatographic resin to separate Cm from Am has been investigated. This method employs an Eichrom TRU resin and nitric acid. Solutions containing a mixture of Am and Cm have been used to test the capability of this Eicrhom resin to separate these two elements, and operating conditions such as column length, flow rate, and elution conditions have been developed. Separation efficiency parameters such as resolution, plate height, and numbers of theoretical plates for the various operating conditions will be presented and discussed.

6-S4-7 20615

THE EXTRACTION OF ACTINIDES WITH DIAMIDES OF DIPICOLINIC ACID

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In the past two decades, amide and diamide ligands have been investigated as possible complexants for reprocessing high-level wastes in order to perform partitioning and transmutation. Diamides derived from dicarboxylic acids have been given attention due to their good extraction ability toward lanthanides and actinides, as well as selectivity for the 5f metals through soft donor nitrogen coordination. Among recently studied ligands, diamidic derivatives of dipicolinic acid have been studied as a possible substitute for CMPO in the UNEX (Universal Extraction).[1] The *N,N'*-diethyl-*N,N'*-ditolyl-dipicolinamide derivative has shown great promise in its ability to extract actinides such as americium from acidic aqueous solutions, as well as providing reasonable separation factors from the lighter lanthanides.

This work will include of an overview of the separations that can be achieved for the actinides using each of the three structural isomers of EtTDPA. In this study it was shown that EtTDPA shows highest affinity for tetravalent actinides, with distribution ratios of plutonium and thorium orders of magnitude above the other actinides under similar conditions. A comparison of separations between newly and previously studied actinides and lanthanides is given. Development of this research could lead to a single extraction mixture for use in the UNEX partitioning scheme.

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6-TS7-8 16905

ORGANOMETALLIC ACTINIDE CHEMISTRY: NEW PLATFORMS FOR MANIPULATION AND ELUCIATION OF MOLECULAR AND ELECTRONIC STRUCTURE

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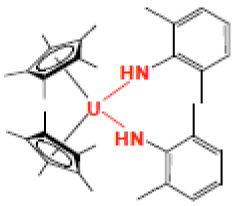
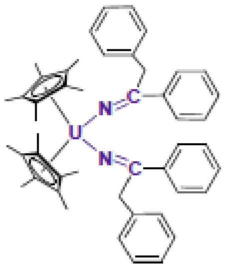
Our understanding of electronic structure and bonding in the light actinide elements has benefited enormously from spectroscopic investigations of classical actinide coordination complexes such as the halide systems (e.g., UCl_6^{2-}) in high symmetry coordination environments. Similarly, evidence for actinide metal – ligand covalent bonding has evolved principally from investigations of the trans-dioxo actinyl (AnO_2^{n+}) ions in a variety of different equatorial coordination environments. While these more classical structural motifs underpin the establishment of relationships among electronic structure, bonding, and spectroscopic observables, they comprise a fairly limited range of metal-ligand bonding interactions, and they provide little versatility or control to rationally design new molecular structural types having variable metal oxidation states and metal nuclearities.

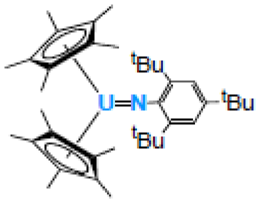
Organometallic chemistry provides an ideal platform for varying ligand sets, structural (symmetry) types, and bonding modalities. Our efforts over the past decade have focused on expanding the known organometallic chemistry of the light actinides, specifically complexes having the $[(C_5Me_5)_2An]^{n+}$ bentmetallocene core [An = Th(IV), n = 2; An = U(III, IV, V, and VI), n = 1 - 4], to encompass mono- and multimetallic systems with ligand sets in the metallocene wedge that span the metal-ligand bonding continuum from simple dative interactions to *bona fide* metal-ligand multiple bonds. One simple example is shown below illustrating the variability in uranium-nitrogen bonding for a U(IV) metal center across the ligand series; amide, ketimide, imide.



$U\text{-}N_{amide} = 2.267(6)$ Å



$U\text{-}N_{ketimide} = 2.184(3)$ Å



$U\text{-}N_{imide} = 1.952(12)$ Å

This presentation will focus on our recent efforts that include developing and characterizing an extensive range of complexes of the uncommon pentavalent uranium oxidation state as well as bi- and trimetallic complexes possessing exclusively actinide metals or a mixture of actinide and lanthanide metals. Throughout this course of synthesis and characterization we have endeavored to correlate electronic spectroscopic data (transition types, band energies and intensities) and metal-based redox data with the molecular structural data to establish signatures for the existence and extent of metal-ligand covalent bonding and to assess metal-metal interactions in multimetallic systems.

NOVEL MAGNETISM AND SUPERCONDUCTIVITY IN ACTINIDE-BASED INTERMETALLIC COMPOUNDS

Yoshinori Haga, Dai Aoki, Dai Aoki, Shugo Ikeda, Tatsuma D. Matsuda, Naoyuki Tateiwa, Etsuji Yamamoto, Akio Nakamura, Kunihisa Nakajima, Yasuo Arai and Yoshichika Onuki

Actinide intermetallic compounds are known to show a variety of physical properties. Particularly the coexistence of superconductivity and long-range antiferromagnetic ordering in UPd_2Al_3 [1], multiple superconducting phases in UPt_3 [2], hidden-order and superconductivity in URu_2Si_2 [3] have attracted attentions for years. Recently, experimental study has been extended to transuranium compounds. The discovery of several new materials showing superconductivity such as $PuCoGa_5$ [4], $PuRhGa_5$ [5] and $NpPd_5Al_2$ [6] have demonstrated that new compounds with novel phenomena are still hidden in the actinide intermetallics.

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AN OPTICAL SPECTROSCOPY INVESTIGATION OF ENVIRONMENTAL EFFECTS ON URANIUM OXYFLUORIDE PARTICLES

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Uranium oxyfluoride (UO_2F_2) is the first metastable hydrolysis product of uranium hexafluoride (UF_6), an important chemical in the uranium separation process as well as a trace impurity in WF_6, which is commonly used in the manufacture of integrated circuits. Due to the high reactivity of UF_6 to moisture, moisture in air is sufficient to initiate hydrolysis, and, after formation of UO_2F_2, hydrolysis continues at a slow rate until all the fluorine atoms are removed from the molecule. Investigation of the rate of fluorine loss is important in nuclear forensic investigations. Understanding how environmental conditions might affect this rate can verify whether a facility is compliant with a facility or State declaration under IAEA safeguards. In our work, UO_2F_2 particles were deposited on various substrates including sapphire, zinc selenide and graphite, and then exposed to pre-defined levels of UV-light, humidity, and temperature. After different exposure times, samples were harvested and analyzed by optical and mass spectrometric techniques to determine the composition, morphology, and structure of the uranium-bearing particles and to see if these properties can be used to estimate duration of environmental exposure. In this talk we will focus on the cryogenic laserinduced time-resolved U(VI) fluorescence microspectroscopy (CLIFS) results obtained at PNNL, which were used to monitor changes in the molecular structure through changes in fluorescence spectra and lifetimes. Additional data from PNNL (Raman and SIMS analysis) and LLNL (Nano-SIMS and SEM analysis) will be presented.

6-S7-11 19696

RECENT COMPUTATIONAL STUDIES OF ACTINIDE COMPLEXES AND THEIR REACTIONS

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The objective of this talk is to discuss the recent progress on computational actinide science with specific emphasis on complexes of U(VI), Np(V), Pu(VI) and Cm(III) that occur in geochemical and biochemical environments and thus such studies are critical to the environmental management of highlevel nuclear wastes [1-5]. We will also be discussing computational modeling of surface chemistry of reactions of actinides with emphasis on three-dimensional charge topographic maps called Laplacians which provide considerable insight to the reactive regions of actinide surfaces [6-7]. Our computational work will be discussed in light of collaborative experimental studies using time-resolved laser fluorescence spectroscopic studies on actinide complexes carried out at Berkeley [2]. One of the primary focal points of this talk would be computational modeling of environmental actinide complexes such as uranyl, neptunyl, and plutonyl complexes with hydroxides, carbonates and silicates [1,3-5] that have being studied in aqueous solution both experimentally and computationally so that we can compare the computed geometries and spectra with known experimental data.

We have recently carried out computational and TRLFS studies [2] on the complexes of curium(III) with multidentate Phosphonopropionic (PPA) acid ligands. A number of complexes of Cm(III) with these ligands, such as CmH_2PPA^{2+}, $CmHPPA^{+}$, $Cm[H_2PPA]_2^{+}$, and $Cm[HPPA]_2^{-}$ have been studied. Our computational studies focused on all possible isomers in the gas phase and aqueous solution so that the relative binding strengths of different ligands. The solvation effects play an important role in the determination of the preferred configurations and binding propensities of these complexes as function of the ligands. Our computations assess the relative strengths of single and multidentate complexes in solutions for these systems. The computed free energies of solvation explain the experimentally observed fluorescence spectra and the lifetimes of these complexes in that as more water molecules are displaced from the first hydration sphere by the ligands that bind to the actinides, the fluorescence lifetime increases. The relative stabilities of these complexes are found to vary substantially between the gas phase and solution, indicating a major role of solvation in the relative stabilities of these complexes. We shall also discuss the recent computational models together with experimental works on functionalized nanomaetrials and mesoporous material interactions with actinides in high-level nuclear wastes. Such mesoporous cages when functionalized with suitable ligands can effectively bind specifically to desired oxidation state of a given actinide. The final part of our talk will focus on computational modeling of surface reactions of actinides and comparison with any experimental results available on these systems.

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6-S7-12 12965

ELECTROSPRAY AND GAS-PHASE BEHAVIOR OF CERIUM PHOSPHOMOLYBDATES: A PRELUDE TO PLUTONIUM CHEMISTRY

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Polyoxometalates (POMs) receive special attention from a fundamental standpoint and due to their applications in medicine, materials science, industrial processes, and nuclear waste remediation[1]. The potential use of polyoxometalates as sequestration/separation agents of *f*–block elements in the nuclear fuel cycle has spawned in–depth surveys into their solution and solid state speciation[2]. However a void exists with regard to the gas-phase chemistry of polyoxometalate-stabilized *f*–block elements. Electrospray-ionization/mass spectrometry (ESI/MS) is proving to be a successful and facile way of transferring these complexes from solution to gas. Current studies are under way to understand the behavior of tri- and tetravalent cerium lacunary-phosphomolybdates during the ESI process and subsequently in the gas phase.

Aqueous solutions of the ammonium salts of $Ce(PMo_{11}O_{39})_2^{n-}$, where n = 10 and ll for Ce(IV) and Ce(III), respectively, serve as source materials for this investigation. Four prominent species, $H_2PMo_{12}O_{40}^-$, $PMo_{13}O_{42}^-$, $Ce(PMo_{11}O_{37})_2^{2-}$, and $Ce(PMo_{12}O_{40})_2^{2-}$, appear in the ESI/MS in the former system. $CePMo_{11}O_{38}^-$ and $PMo_{13}O_{42}^-$ are produced in highest yield in the latter. Important to note here is that Ce(III) does *not* seem to transfer to the gas phase as an intact sandwich-complex but rather accompanied by only one pseudo-lacunary POM and the formal valent state of resulting Ce(III)-POM species is +4. This activity is clearly complex and not yet understood. Multiple individual cluster series of the following compositions are present irrespective of initial cerium valence: $HMo_aO_{3a+1}^-$, $Mo_bO3_{b+1}^{2-}$, $PMo_cO_{3c+3}^-$, and what is tentatively described as $CeO_2PMo_dO_{3d+3}^-$. As the stabilization of tetravalent cerium through the electrospray process is rare[3], the significance of these results gives hope that similar conditions will facilitate analogous plutonium gas phase studies. As such, this work will serve as a stepping stone towards the development of a methodology for transuranium explorations.

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TIME-RESOLVED LASER FLUORESCENCE MICROSCOPY (TRLFM) FOR ADSORPTION STUDY OF LUMINESCENT F-ELEMENT ON A HETEROGENEOUS SURFACE

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Time-Resolved Laser Fluorescence Microscopy (TRLFM) is a useful tool to simultaneously investigate the intensity, location, type and surrounding chemical environment of luminescent f-elements. In this study, we demonstrate the applicability of TRLFM for the adsorption of Eu(III) on a natural heterogeneous surface. Different adsorption species of Eu(III) are observed on the Makabe granite surface and its constituents (biotite, plagioclase, potassium feldspar and quartz). Eu(III) heterogeneously adsorbed on biotite, plagioclase and quartz and homogeneously on potassium feldspar. The histograms of the fluorescence decay rates of adsorbed Eu(III) indicates efficient quenching of Eu(III) fluorescence probably due to Eu(III)-surface interaction or the formation polynuclear hydoxo Eu(III) species on the surfaces. It is also revealed that single species of Eu(III) is observed on biotite and two species on plagioclase and potassium feldspar. The adsorption of Eu(III) on the granite surface is highly heterogeneous. The TRLFM measurements of different regions of the granite surface suggests the presence of Eu(III) species with different fluorescence decay rates. Comparing with the fluorescence decay histograms of the mineral constituents, it is shown that Eu(III) clearly adsorbs on the feldspar family. It is also found that Eu(III) adsorbs as an outer-sphere complex and on an altered mineral of the granite.

7-PS5 17457

SUPERHEAVY ELEMENT RESEARCH AT TASCA

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The superheavy element (SHE) research program has successfully started at the newly built and fully commissioned TransActinide Separator and Chemistry Apparatus (TASCA) [1,2] with an experimental program focusing on element 114. The TASCA project concentrates on the separation and investigation of neutron-rich transactinide nuclides produced in actinide target based reactions. It includes chemical investigations of SHE after preseparation with the gas-filled separator and nuclear structure and nuclear reaction studies. The central device of TASCA is a gas-filled separator in a Dipole-Quadrupole-Quadrupole (DQQ) configuration operated either in the "High Transmission Mode" (HTM, DQ_hQ_v) or in the "Small Image Mode" (SIM, DQ_vQ_h) [1-5]. In the HTM, the unsurpassed transmission of TASCA is exploited. In contrast, the SIM provides unique possibilities due to its small spot size in the focal plane. Extensive studies have been performed to obtain optimized parameter sets for target thicknesses, gas pressures and filling gases (He, H_2, and mixtures), dipole settings (for magnetic rigidities) and quadrupole focusing, Recoil Transfer Chamber (RTC) designs [6], gas-jet transport of preseparated products, and the coupling and performance of external devices like ROMA and ARCA. Experimental results showed very good agreement with model calculations [7]. To obtain a standard reaction to check the TASCA performance, detailed studies were performed with well known reactions of ^{48}Ca with targets of ^{206,207,208}Pb leading to ^{252,253,254}No [8]. Efficiencies of 54%, 56%, and 50%, respectively, were obtained for the HTM using a (80x36) mm2 focal-plane detector; model calculations [7] predict 54%. In the SIM 30% efficiency was measured for ^{254}No. As another crucial test, we studied the isotopes $^{260\text{-}262}$Rf synthesized in the very asymmetric reaction ^{22}Ne + ^{244}Pu [9]. The performance of TASCA was as anticipated. Rf isotopes were also transported to ROMA for decay measurements [9] and to ARCA for the first aqueous-phase transactinide chemistry behind TASCA [10]. Results of the first highlight of the scientific program at TASCA -the first synthesis, separation and investigation of element 114 isotopes produced in ^{48}Ca on ^{244}Pu reactions at GSI -will be discussed and will be compared with results obtained at Dubna [11].

7-PS6 17734

LOOKING FOR THE EFFECT OF TENSOR FORCES IN NUCLEI

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Recent studies of nuclei far from the stability line show systematic changes of shell orbitals. In some cases new magic numbers are formed and also disappearances of the traditional magic numbers are seen. It is considered that the tensor forces in nucleonnucleon interactions may give an important contribution on such effects.

The tensor forces were known to be important for binding light nuclei such as ^{4}He through a D-wave mixing. It was also considered to play important role for the deviation of the isoscaler magnetic moments of doubly closed shell±1 nuclei. However no direct evidences of the effect of tensor forces has not been seen in nuclear wave function.

Recent experimental project of searching for effects of the tensor forces will be discussed and new data from RCNP will be presented.

7-PS11 22336

MICROANALYTICAL ^{14}C AMS MEASUREMENTS ON CARBONACEOUS PARTICLES

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Carbonaceous aerosols are increasingly recognized as important atmospheric constituents. These small atmospheric particles - including black carbon (BC) and organic carbon (OC) - are produced by incomplete combustion of fossil fuel, biofuel and outdoor biomass.

Current investigations aim at a partitioning of BC and OC to biogenic and anthropogenic sources to improve our knowledge on the contribution of each fraction to the ambient atmosphere. One option to determine the two contributions is a determination of the ^{14}C concentration. The ^{14}C activity in ambient, biogenic carbon is 227 Bq/kg C and the corresponding atomic ratio for $^{12}C/^{14}C$ is approx. 10^{12}:1. On the other hand ^{14}C is extinct in carbon from fossil fuel sources.

Measurements of ^{14}C in atmospheric aerosol samples require techniques applicable to about 10 microgram of total carbon, given the low mass concentration of such particles in the atmosphere. Radioanalytical techniques fail to achieve this sensitivity and even classical accelerator mass spectrometry requires milligram amounts of carbon.

We have therefore developed a novel procedure able to on-line determine ^{14}C from a few microgram of total carbon that can be coupled to a gas-ion source of the Mini-Tandem System MICADAS operated at only 200kV voltage.

In the presentation some application of this technique to atmospheric studies as well as to nuclear dating of e.g. glacier ice used for climate studies are outlined.

8-TS7-1 21199

HYBRID MATERIALS FROM THE AN ELEMENTS: SYNTHESIS, STRUCTURE, AND SPECTROSCOPY

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Uranyl containing coordination polymers and metal-organic framework ('MOFs') materials exhibit tremendous structural diversity owing not only to a rich local geometry about the UO_2^{2+} centers, but also as a result of uranyl hydrolysis and the formation of polymeric secondary building units (SBUs).[1] Beyond monomers, uranyl containing dimers through pentamers have been observed that when polymerized through organic 'linker' molecules, give rise to a range of one-, two- and three-dimensional structures.[2] Presented will be a systematic overview of UO_2^{2+} inorganic/organic hybrid materials as well as our efforts to control hydrolysis and ultimately influence SBU speciation. For the latter, we explore pH and the use of highchloride media. Many synthesis reactions take place under hydrothermal conditions, which not only promote hydrolysis, but also facilitate redox within the organic components. Such redox often results in '*in-situ* ligand synthesis,' wherein oxidation or decomposition of intended linker molecules provides a range of species not present at the onset of a reaction.

A related approach to the formation of Np containing hybrid materials can be applied as well. In this system however, more facile redox and the formation of cation-cation interactions in Np(V) compounds allows for additional diversity and modes of connectivity. Specifically, aqueous reactions of Np(V) with squaric acid as a function of pH and temperature yield a Np(IV) oxalate, a Np(IV) oxalate/squarate and a Np(V) squarate. The latter of these exhibits an unprecedented hexameric 'wheel' of of Np(V) centers connected through cation-cation interactions.

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THE SURFACE CHEMISTRY OF COLLOIDAL PLUTONIUM

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Colloidal metal oxide phases are known to have significant roles in the transport and migration of metal contaminants in the environment as well as in the reprocessing of spent nuclear fuel especially by solvent extraction methods. Single crystal X-ray diffraction data complemented by X-ray scattering studies demonstrated that the colloid of plutonium is based upon discrete nanometer sized clusters of plutonium dioxide with a surface truncated by simple inorganic anions. Key to assessing the risk associated of colloidal plutonium transport in the geosphere and understanding its behavior in separations chemistry is an understanding of the surface reactivity of the particle itself.

This presentation will focus on recent experimentation with the surface reactivity of plutonium colloids, which has demonstrated that the surface anion stoichiometry is dynamic and the anions at the surface are labile. The reactivity of the surface anions and our ability to exchange them allows for the changing of both the overall charge of the colloid as well as the chemistry and reactivity of the plutonium colloids in solution with significant implications for subsurface transport pathways including sorption and precipitation. Evidence for these surface exchange reactions is observed both in the solid state as well as in the changing optical spectra of the plutonium colloids in solution. Our ability to exploit these exchange reactions and the surface reactivity of plutonium colloids in order to chemically manipulate and design their solution behavior will be discussed with an emphasis on separations.

This work was performed at Argonne National Laboratory operated by UChicago Argonne LLC for the United States Department of Energy Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under contract DE-AC02-06CH11357

8-S7-3 21871

RELATIVISTIC DFT INVESTIGATIONS OF NMR PROPERTIES OF ACTINIDE COMPOUNDS

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NMR spectroscopy is vital in providing important information for actinide compounds. The difficulty of experimentation with radioactive samples combined with the difficulty of interpreting results from molecules containing heavy nuclei have to date deterred its widespread utilization in actinides research. We have investigated the NMR properties of several selected actinide compounds, including uranyl complexes and thorium and plutonium species. Relativistic density functional theory was employed to determine the NMR properties. Two-component zero-order-regular-approximation was applied to take into account scalar relativistic effects and spin-orbit coupling effects. Systematic investigations were carried out on the dependence of the calculated ligand nuclear shieldings, chemical shifts, and electric field gradients on the relativistic models, atomic local basis functions, the geometric structures used, and the electron correlation models, particularly the performance of different exchange-correlation functionals on calculating NMR properties of actinide compounds. We conclude that with appropriate selection of the DFT methods and accurate account of relativistic effects NMR properties can be reproduced with reasonable accuracy through theoretical chemistry computations.

8-S7-4 15842

PLUTONIUM OF NAGASAKI ATOMIC BOMB DEPOSITED AROUND NAGASAKI, JAPAN

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Plutonium isotopes were released from Nagasaki atomic bomb which exploded on August 9, 1945. The isotopes are interesting in research on environmental radioactivity, because evident information of the plutonium release provide opportunities to simplify understanding of environmental behavior of Pu. The Nagasaki area is one of the oldest areas that were contaminated with the artificial Pu in the world, and since then, atmospheric nuclear tests have been carried out worldwide, which resulted in additional Pu inventory as global fallouts. Thus Pu in Nagasaki area is a mixture of the Pu from the atomic bomb and that from the global fallout. Discrimination of the Pu due to atomic explosion in Nagasaki from global fallout Pu is required in order to understand the behavior of the Pu from the atomic bomb. As the isotopic composition of Pu depends on its origin, ^{240}Pu/^{239}Pu ratio is a useful tool for the identification of the source of Pu. This paper is intended to report the ^{240}Pu/^{239}Pu ratios in sediments and surface soils and distribution of the Pu from the atomic bomb.

The sediment cores were collected at Nishiyama reservoir in Nagasaki city, which experienced the 'black rain' formed from the detonation of the atomic bomb and the depth profiles of ^{240}Pu/^{239}Pu ratio and $^{239+240}$Pu concentration in the cores were determined to obtain depositional record of Pu released from the atomic bomb for 60 years. Identified were the sediments containing deposition from the atomic bomb, which was accumulated at 1945. The profiles also revealed that the Pu from the atomic bomb were deposited abruptly after the detonation and then were continuously being deposited together with those from the nuclear tests even at present.

In order to determine geographical distribution of Pu from the atomic bomb, the ^{240}Pu/^{239}Pu ratio and the $^{239+240}$Pu concentration were measured in surface soils collected around the hypocenter of the atomic bomb. The ^{240}Pu/^{239}Pu ratios lower than the global fallout value were found in soils collected at the Nishiyama, at the eastern area of Nagasaki prefecture and even at northern part of Kumamoto prefecture. This disclosed that the Pu from the atomic bomb was deposited between 2 km and about 100 km east from the hypocenter.

HIGH-SENSITIVE MEASUREMENT OF U L_{III}-EDGE X-RAY ABSORPTION NEAR-EDGE STRUCTURE USING BENT CRYSTAL ANALYZER FOR THE DETERMINATION OF THE OXIDATION STATES OF URANIUM IN CRUSTAL MATERIALS

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It is important to predict the migration of U in natural environments from various reasons. In particular, the identification of the chemical state of elements, that is, the speciation, is of great importance in order to understand the geochemical processes in natural samples. This is because the chemical state controls the behavior of elements in the environment. In the case of U, the oxidation state is primarily important due to the much different solubilities between insoluble U(IV) and soluble U(VI). For the speciation of a trace element in solid samples, X-ray absorption fine structure (XAFS) has been widely used due to its applicability to almost all elements in various phases and its relatively high sensitivity. In particular, many studies have applied XAFS for the speciation of U in synthetic systems that simulated the natural environment. However, the direct speciation of U in natural samples by XAFS remains difficult possibly due to the spectral interferences by major chemical components such as Rb and Sr.

In this study, X-ray absorption near-edge structure (XANES) spectra at uranium L_{III}-edge XANES were measured for uranium in natural rocks at the uranium concentration range of 0.96–124 mg/kg using a log spiral bent crystal Laue analyzer (BCLA) combined with a multi-element Ge detector. It was found that the quality of the XANES spectra using the BCLA was greatly improved due to the reduction of interfering fluorescence from major components such as Rb and Sr (> 100 mg/kg). The ratio of signal to background intensities in the U L_{III}-edge XANES spectra increased by a factor of 2.9–17 with the use of the BCLA, which greatly lowered the detection limit of U for the determination of the oxidation states, or the U(IV)/U(VI) ratio, in natural samples. In addition, it was also demonstrated that the fluorescence XANES method coupled with the BCLA can be used for the determination of the speciation of U for various natural samples such as acidic igneous rocks, ferromanganese nodules, sediments, and some sedimentary rocks such as shale and limestone. In the presentation, more example of measurement of fluorescence XAFS using bent crystal analyzer for trace elements will be given.

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8-S7-6 19130

TRENDS IN Ln(111) SORPTION TO DEFECT RIDDEN QUARTZ: INSIGHTS FROM A MULTISCALE COMPUTATIONAL APPROACH

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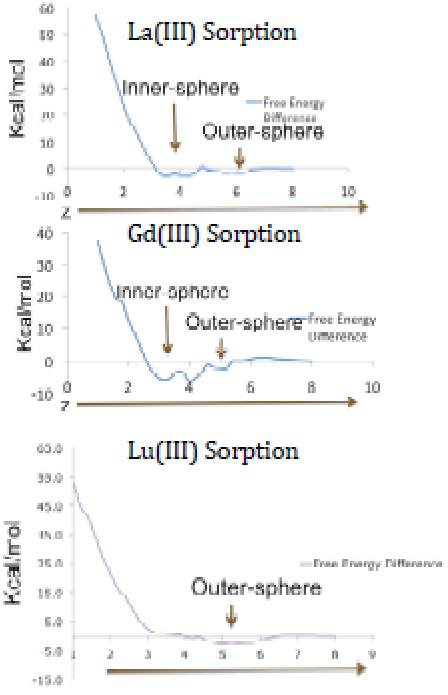
A holistic approach has been taken toward understanding the fundamental features of Ln(III) sorption to mineral surfaces using a multiscale computational approach that spans molecular quantum mechanics (QM) to bulk classical dynamics (MD). The first key aspect of understanding ion sorption lies in accurately describing the ion in bulk solution. Thus, the aqueous behavior of Ln(III) was investigated using density functional theory (DFT), where the free energies of hydration and structure of the primary and secondary hydration shells were benchmarked against experimental values.[1-3] Using the QM potential energy surfaces for water exchange/dissociation from the primary hydration shell of Ln(III) classical force-fields were fit that enabled investigation of the dynamic features of Ln(III) hydration in bulk water. These MD results satisfactorily reproduced the primary solvation features.



The second key element toward understanding ion sorption lies in characterizing the physical properties of the water:mineral interface. Here, MD and periodic boundary DFT calculations have been used to ascertain the dielectric and structural features of water on a quartz surface under different saturation conditions. The dielectric of monolayer water coverage in quartz and its structural immobility were benchmarked against experimental data, with excellent agreement between the theoretical and experimental values.[4]

With a fundamental understanding of both ion behavior in bulk water, and the water:quartz interface, the key features of ion sorption to a mineral surfaces have been examined. Potential of mean force simulations were performed along a sorption coordinate of the ion from the bulk, through the interfacial water, and to the surface of α-quartz. The free energies and structures of sorbed ion species were determined as a function of different prototypical defects on the quartz surface. The simulations indicate a clear trend in 1) strength of the ion:mineral interaction, and 2) the preference of inner- vs. outer sorbed species, as a function of the free energy of hydration of the ion (Figure) and surface charge density of the ion. The success of these simulations poise us well to study more complicated systems like the actinides, where redox behavior and a more complex electronic structure will likely alter sorption features. This holistic approach highlights the predictive power of multiscale computational methods to complement experimental studies of ion sorption processes.

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9-TS5-1 15292

PRESENT STATUS AND PERSPECTIVES OF SUPERHEAVY ELEMENT CHEMISTRY AT RIKEN

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Present status and perspectives of superheavy element (SHE) chemistry at RIKEN are reviewed. A gas-jet transport system for SHE chemistry has been coupled to the gas-filled recoil ion separator GARIS at the RIKEN Linear Accelerator (see Fig. 1). This system is a promising approach for exploring new frontiers in SHE chemistry: (i) the background radioactivities of unwanted reaction products are strongly suppressed, (ii) the intense beam is absent in the gas-jet chamber and hence high gas-jet efficiency is achieved, and (iii) the beam-free condition also allows for investigations of new chemical systems. We have systematically investigated the performance of the system using 206Fr, ^{245}Fm, ^{255}No, ^{261}Rf, and ^{265}Sg produced in the ^{169}Tm(^{40}Ar,3n), ^{208}Pb(^{40}Ar,3n), ^{238}U(^{22}Ne,5n), ^{248}Cm(^{18}O,5n), and ^{248}Cm(^{22}Ne,5n) reactions, respectively [1–4]. Alpha-particles of these nuclides separated with GARIS and extracted to a chemistry laboratory were successfully identified with the rotating wheel system MANON for α-spectrometry. A gas-chromatograph column directly coupled to GARIS, which enables in-situ complexation and isothermal gas-chromatography of a large variety of volatile compounds of SHEs, is under development. On the other hand, a conventional gas-jet coupled target system was installed on a beam line of the RIKEN AVF Cyclotron to extend the detailed aqueous chemistry of Rf and Db at JAEA [5] to heavier SHEs. The gas-jet transport of reaction products to the chemistry laboratory was examined with ^{255}No, ^{261}Rf, and ^{265}Sg produced in the ^{248}Cm(^{12}C,5n), ^{248}Cm(^{18}O,5n), and ^{248}Cm(^{22}Ne,5n) reactions, respectively [6]. Micro-chemical devices for ion exchange and solvent extraction are under development together with a gas-jet coupled dissolving unit and an automated α-particle detection system. In the symposium, a chemistry program at RIKEN will be also presented.

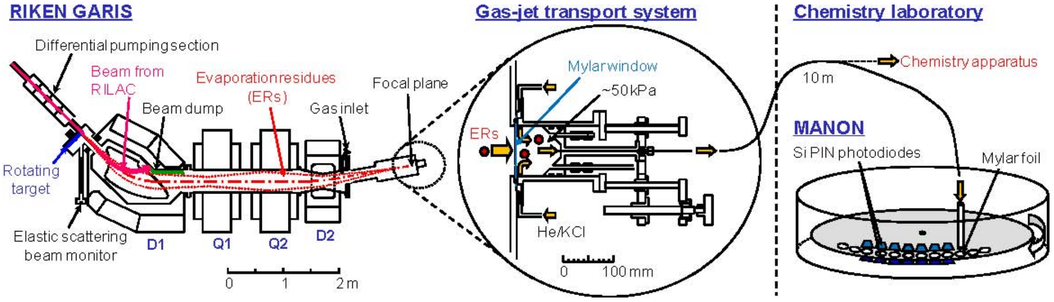

Fig. 1. Gas-jet transport system coupled to the RIKEN gas-filled recoil ion separator GARIS and a rotating wheel apparatus MANON for α spectrometry placed at a chemistry laboratory.

ESTIMATING SUPER HEAVY ELEMENT EVENT RANDOM PROBABILITIES USING MONTE CARLO METHODS

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Because superheavy element (SHE) experiments involve very low event rates and low statistics, estimating the probability that a given event sequence is due to random events is extremely important in judging the validity of the data. A Monte Carlo method developed at LLNL [1] is used on recent $^{48}Ca+{}^{226}Ra \rightarrow 108$ experimental data to calculate random event probabilities. Since the actual experimental data is used in determining the random event probabilities, fluctuations in experimental conditions, such as in background or electronic noise, during the months of continuous beam time are automatically included in this method, whereas such important fluctuations may not be included in methods based on average rates during the experiment. Random EVR-SF, EVR-alpha-SF, and EVR-n alphas-SF event rates are 1.7×10^{-2}, 1.3×10^{-4} and 2×10^{-7}, respectively. Including Geiger-Nuttall systematics reduces these rates even further. Current SHE experimental activities in collaboration with scientists at Dubna, Russia will be discussed.

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UNDERSTANDING (SUPER)HEAVY ELEMENT CROSS SECTIONS

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The production and decay of element 114 isotopes has been observed with the Berkeley Gas-filled Separator at the Lawrence Berkeley National Laboratory 88-Inch Cyclotron. One atom each of ^{286}114 and ^{287}114 were produced in ^{242}Pu(^{48}Ca,3-4n)$^{286\text{-}287}$114 reaction. Observed decay modes, decay energies, and lifetimes agree with those published by the Dubna Gas Filled Recoil Separator Group [1].
A series of excitation functions have been measured using ^{238}U targets with neutron-rich projectiles from ^{22}Ne through ^{37}Cl. These excitation functions have been used to determine details of the reaction mechanism for heavy element formation via compound nucleus formation followed by de-excitation by neutron emission in competition with fission. Deduced values for critical angular momentum for fusion , l_{crit} , and the ratio of fission width to total decay width, Γ_n / Γ_{tot} , will be presented. Implications for the constant picobarn-level cross sections observed for superheavy element formation will be discussed.

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NUCLEAR CHEMISTRY OF ACTINIDES AND TRANSACTINIDES AT IMP

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Many efforts have been made in IMP (Institute of Modern Physics) to synthesize neutronrich actinides in last 15 years, several new isotopes, such as ^{237}Th, ^{238}Th, ^{239}Pa were produced via ^{18}O-induced multinucleon transfer reaction at Heavy Ion Research Facility at Lanzhou. Fast chemical separation procedure based on solvent-extraction has been widely used to isolate thorium and protactinium from the bulk of uranium target material. The growth and decay of the γ-rays of the daughter nuclei have been applied to identify the new isotopes as a parent. Americium fraction were chemical separated rapidly from fission products, and a new neutron-deficient americium isotope of ^{235}Am was also synthesized and identified in the reaction of ^{238}Pu (p, 4n).

Two new transactinides isotopes of ^{259}Db and ^{265}Bh were successfully synthesized by using helium-jet technique coupling with a rotating wheel apparatus. A new isotope of ^{259}Db has been produced via the reaction ^{241}Am(^{22}Ne, 4*n*) at *E*lab = 118 MeV, and its half-life of 0.51±0.16 s and α-decay energy of 9.47 MeV were determined. Another new isotope of ^{265}Bh has been produced via the reaction ^{243}Am(^{26}Mg, 4*n*) at *E*lab = 168 MeV, and its half-life of 0.94±0.16 s and α-decay energy of 9.24 MeV were determined. The identification of ^{259}Db was performed based on the genetic relationship between the new activity and the known ^{255}Lr established by α-recoiled milking measurement. Identification of ^{265}Bh was made by observation of correlated α-particle decays between the new isotope ^{265}Bh and its ^{261}Db and ^{257}Lr daughter nuclei. A total of 8 correlated decay events of ^{265}Bh have been observed.

As the start-up of the chemistry of transactinides at IMP, an isothermal chromatography apparatus, which is similar to OLGA-III, have been developed for the homologues of transactinides. Test experimental results show short-lived Tc isotopes can be rapid separated in the form of TCO$_3$ from the fission products of ^{252}Cf with high efficiencies using high temperature isothermal chromatography apparatus. Only short lived isotopes of Tc and its daughter were observed in the γ-spectrum. The adsorption enthalpy of TcO$_3$ on the quartz surface were determined to be -150±5 kJ/mol, it consistent with the literature data. Gas chemistry of group 5 elements Nb and Ta with bromine have been tested with short-lived isotopes of ^{88}Nb and ^{170}Ta which produced with ^{19}F beam in bombardment with Ge and Gd targets. The results show that pure brominates compounds were formed as pure HBr as a reactive gas. The adsorption enthalpy of NbBr$_5$ and TaBr$_5$ on the quartz surface were determined to be -89 ± 5 kJ/mol and -105 ± 5 kJ/mol, respectively. The gas-phase chemistry of Dubnium which will produced via ^{243}Am(^{20}Ne,5n)^{258}Db will be performed by end of year.

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ELECTROCHEMISTRY OF THE HEAVIEST ELEMENTS AT JAEA

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It is of great importance to study oxidation-reduction (redox) properties of the heaviest elements for understanding relative stabilities of each oxidation state and also structure of valence electrons that would be affected by relativistic effects. Recently, we have developed an electrochemistry apparatus combined with a chromatographic separation technique available for single atom chemistry [1]; glassy carbon fibers modified with Nafion perfluorinated ion-exchange resin are employed as a working electrode as well as a cation exchanger. In this paper, electrochemical oxidation of element 102, nobelium (No), in 0.1 M α hydroxyisobutyric acid (α-HIB) using the apparatus will be presented [2]. The isotope ^{255}No with a half-life of 3.1 min was synthesized in the ^{248}Cm(^{12}C, 5*n*) reaction at the JAEA tandem accelerator with a typical production rate of 30 atoms/min. Reaction products were transported to a chemistry laboratory by a He/KCl gas-jet method and were then deposited on a plastic plate of a rapid chemistry assembly for 10 min. After collection, the products were dissolved with 0.1 M α-HIB (pH 3.9) and subsequently fed into the working electrode packed in a porous Vycol glass tube. As a counter electrode, a Pt mesh was used to surround the glass tube in α-HIB solution. The potential applied to the working electrode was adjusted to 0.2-1.2 V vs. a Ag/AgCl electrode in 1.0 M LiCl. The effluent from the column electrode was consecutively collected with a volume of 180 μL on six separate Ta discs. The remaining products in the column were stripped with 360 μL of 3.0 M HCl and collected on another two Ta discs. The eight samples were evaporated to dryness using hot helium gas and halogen heat lamps and were then transferred to an α-spectrometry station equipped with eight 600 mm^2 passivated implanted planar silicon detectors. The ^{248}Cm target contained Gd to simultaneously produce ^{162}Yb as the representative trivalent ion through the Gd(^{12}C, *x*n) reaction. After the α-particle measurement for No, the discs were assayed by γ-ray spectrometry with a Ge detector to monitor the elution behavior of ^{162}Yb$^{3+.}$ The elution behavior of ^{81}Sr and ^{162}Yb produced in the Ge(^{12}C,*x*n) and Gd(^{12}C, *x*n) reactions, respectively, was also investigated to establish a clear separation between divalent (Sr$^{2+)}$ and trivalent (Yb^{3+}) ions in the present system.

In the experiment with ^{81}Sr and ^{162}Yb, ^{16}2Yb^{3+} was eluted with 0.1 M α-HIB while ^{81}Sr^{2+} was present in the subsequent strip fraction of 3.0 M HCl; clear separation between the trivalent and divalent ions was confirmed. At 0.2 V, ^{255}No was detected in the 3.0 M HCl fraction while the monitored ^{162}Yb^{3+} was eluted earlier with α HIB. The adsorption of ^{255}No was the same as that of ^{81}Sr^{2+}, clearly indicating that No was bound in its stable divalent state. On the other hand, the elution of ^{255}No in the 0.1 M α-HIB fraction was unambiguously observed at 1.2 V at the position of ^{162}Yb^{3+}. This behavior demonstrated that No^{2+} was successfully oxidized to No^{3+} and that the trivalent state was complexed in the α-HIB solution with the present apparatus. Very recently, an electrochemical reduction of Eu^{3+} to Eu^{2+} with a carrier-free ^{146}Eu radiotracer as a model of element 101, mendelevium (Md) was successfully performed. Reduction properties of Md will be investigated using the apparatus.

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PRESENT SITUATION AND FUTURE PROSPECTS ON NUCLEAR AND RADIOCHEMISTRY EDUCATION IN JAPAN

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Research work in any field is affected by the education prospects of the respective fields in both positive and negative ways. I would like to summarize the present situation and future prospects on nuclear and radiochemistry education in Japan with the help of references [1-3] presented on the topics irrespective of the limitation of my scope.

Described below are positive aspects of the educational situations in Japanese universities and research institutes which bear the responsibility of education. Nuclear science is still important in many industry and research fields in relation to nuclear medicine, material science, nuclear power industry and so on.[1] Momentum toward development of human resources is increasing in the nuclear power industry because of international pressure for carbon-oxide reduction and the need for development of nuclear waste treatment in Japan.[2] As a result, engineers, researchers and leaders of research groups have had to gain a broad perspective in energy crisis and environmental problems.

On the other hand, negative aspects are as follows. The number of students in the nuclear field, including radiochemistry, has decreased in recent years in Japan. Tight budgets at universities prevent maintenance of the nuclear facilities in good condition, which has largely discouraged students.[1,2] For a promising prospect of education in the field, a new methodology for human resources development for nuclear science and technology has been proposed by several universities in Japan and Japan Atomic Energy Agency (JAEA), which established the Japan Nuclear Education Network (JNEN) and has started a multi-directional education system among JAEA and several universities.[3] JNEN has established a comprehensive human resources development program by utilizing unique courses at universities and a real-time multi-directional network system as well as effective curriculums with an emphasis on practical exercises by utilizing JAEA's training and experimental facilities. The network aims to implement the JNEN system among JAEA and some universities, improve the JNEN system with obtained experiences and expand the number of participant universities.

The JNEN Distance Education System was initiated in April 2007 and presently connects Tokyo Institute of Technology, University of Fukui, Kanazawa University, Ibaraki University, Okayama University, and Osaka University to JAEA. New programs with unique nuclear courses in each university as common subjects are performed as real-time lectures using large TV screen and Tablet. They enable us to realize real-time "Questions and Answers" sessions between professor and students, real-time discussions among students in participant universities, and also self-directed *e*-learning after lectures. The programs are expected to overcome the unfavorable circumstances described above.

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[3] Y. Fujii, T. Nakanishi, T. Fukui, H. Kato, and H. Ojima, Japan Nuclear Education Network (JNEN), A Multi-Directional Education System among JAEA and Several Universities, Presentation by J. Sugimoto in Conference on Nuclear Training and Education (2009).

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NUCLEAR ANALYTICAL TECHNIQUES FOR NANOTOXICOLOGY STUDIES

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With the rapid development of nanotechnology and its applications, a wide variety of nanomaterials are now used in commodities, pharmaceutics, cosmetics, biomedical products, and industries. The potential interactions of nanomaterials with living systems and the environment have attracted increasing attention from the public, as well as from manufacturers of nanomaterial-based products, academic researchers and policymakers. It is important to consider the environmental, health and safety aspects at an early stage of nanomaterial development and use in order to more effectively identify and manage potential human and environmental health impacts from nanomaterial exposure. However, to date, little is known about the occurrence, fate and toxicity of nanomaterials. The limitations in our knowledge are partly due to the lack of methodology for the detection and characterisation of engineered nanomaterials in complex matrices, i.e. water, soil or animal tissues. Nuclear analytical techniques can play important roles in nanotoxicology studies due to their intrinsic merits such as high sensitivity, good accuracy, high space resolution, ability to distinguish the endogenous or exogenous sources of materials, ability of *in situ* and *in vivo* analysis, etc. In this presentation, we will discuss some latest results of studies on nanotoxicology using nuclear analytical techniques carried out in our Labs.

(i) Establishment of standard sample preparation method for chemical impurity analysis of carbon nanotubes using NAA as a reference method;
(ii) (ii) Measurement of two-dimensional distributions of nanomaterials in animal tissues by SRXRF;
(iii) (iii) Quantitative analysis nanomaterials in biological and environmental samples by radiotracer technique.

PROBING BIO–NANOSCTRUCTURES (DNA) WITH IONIZING RADIATION: PERSPECTIVES FOR IMPROVING CANCER RADIOTHERAPY

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In the conventional treatment of cancer, an ideal radiation source would deliver a near-uniform dose to the target and nothing outside it. This paragon is presently unachievable. More realistically, the challenge is to deliver a fatal dose of radiation to the target volume while minimizing damage to surrounding normal tissue. This is partially achieved in therapy with heavy ion beams, but this alternative is still under development as an effective treatment option in most clinical settings. At present, the most common radiotherapy treatments still use γ rays. Several innovative approaches to improve the efficacy of radiation therapy are in progress.

Here we examine the potential of a strategy designed to reduce radioresistance by means of exogenous static electric fields (SEF). Thus, T47D breast cancer cells were firstly irradiated with 1 and 2 Gy of gamma radiation, and then exposed to a SEF of 1250 V/cm by 24 hours. After these treatments cells cycle distributions were evaluated by flow cytometry. It was found that the treatment with irradiation plus SEF exposure causes a higher accumulation of cells at the S phase, and a corresponding reduction at G1, while the population in G2/M was nearly unchanged.

It is concluded that a SEF negatively interferes in the repairing process and, therefore, this physical agent works as a radiation sensitizer for possible clinical application. Because of the low SEF intensity it could be applied externally and directly to the patient, preferentially during and after the tumor irradiation. Actually, effects on cells simultaneously exposed to ionizing radiation and static electric fields have been recently reported [1], showing that substantial increase in cell death *vis-à-vis* samples only irradiated is achieved. It was suggested that static electric fields could hamper DNA repair processes. In accordance with a biophysical model developed at this Laboratory, an exogenous electric field polarizes the displacement of repair proteins, making their harboring to the DNA damage sites difficult [1].

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THE ROLE OF POLYMERIZATION AND (PSEUDO)COLLOID FORMATION FOR UNDERSTANDING THE BEHAVIOR OF AN IONS IN AQUEOUS SOLUTION

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Polynuclear complexes and colloids play an important role in the aqueous chemistry of tetravalent actinides, particularly hydroxide complexes, which form over a rather wide range of acidities and An concentrations. Recent findings stress the essential role of Pu(IV) polymers and colloids for understanding Pu redox chemistry [1] and it is well known that the presence of colloids affects the so called "disproportionation" of Pu(IV) and Pu(V) [2]. The present work aims at understanding the role of polymers for the redox chemistry of actinide ions in solution, in particular the reactions relevant for the safety assessment of deep geological nuclear waste disposal. At concentrations above [An]=1μM which might occur within the repository (near field) metal hydroxide polymers form even in strongly undersaturated solutions and hence must be considered for understanding the chemistry of Pu. By ESITOF-MS [3], Pu(IV) hydroxide dimeric, trimeric and larger Pu hydroxide complexes were found to form. The data revealed that not all polymers are composed of tetravalent Pu ions. Depending on chemical conditions they contain also tri- and pentavalent Pu ions. This direct observation of mixed valence polymers nicely corroborates earlier evidence of colloids linking the lower oxidation states Pu(III) and Pu(IV) with the dioxo species PuO_2^+ and $PuO_2^{\ 2+}$[1] in Pu redox reactions and also is in accordance with formation of PuO_{2+x} phases. Further growth of these polymers leads to the formation of true colloids, who, in the case of Pu(IV), grow with increasing pH accompanied by increasing Pu-Pu coordination number and increasing order of the Pu sublattice.

In the far field of a repository true colloids might not play the dominant role, but rather transport is governed by formation of pseudocolloids, i.e., radionuclides sorbed onto natural colloids. Within a collaboration with the Swiss Grimsel project (CFM) theses processes are studies by observing the breakthrough of a cocktail of bentonite colloids and Am, Pu, Np and U. In the case of Am(III) and Pu(IV) colloid mediated transport was shown to be the dominant migration mechanism. By measuring not only the mean diameter and total mass of the colloid breakthrough but also the particle size distribution by laser-induced breakdown detection, the metal breakthrough could be correlated to the total colloidal surface.

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APPLICATION OF ACCELERATOR MASS SPECTROMETRY TO ARCHAEOLOGY, GEOGRAPHY, AND ENVIRONMENTAL SCIENCE

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Accelerator mass spectrometry (AMS) is an ultra-senstive method for the measurement of isotope ratios of long lived radioisotope to stable isotope (e.g. $^{14}C/^{12}C \approx 10^{-12}$ - 10^{-15}). The Erlangen AMS facility, which is especially used for radiocarbon measurements, consists of a negative ion source, an injection spectrometer, a 6 MV EN tandem accelerator, an analyzing spectrometer and a heavy ion gas detector. Negative ions are generated from solid or gas samples in a hybrid sputter ion source from NEC, pre-accelerated to 50 keV and injected into the accelerator by a combination of a 90° electrostatic deflector and a 90° magnet with fast isotope switching for the sequential injection of ^{14}C, ^{13}C and ^{12}C ions. At 5 MV terminal voltage the most abundant positive charge state is 4+, which is analyzed in a mass spectrometer consisting of a 15° electrostatic deflector and a 55° magnet. Finally the stable ions ^{13}C and ^{12}C are measured in Faraday cups and ^{14}C is detected in a ΔE-E gas detector, which serves as a last filter for the remaining background. The beam transport between injection- and analyzing magnet is completely performed by electrostatic devices, which ensures identical ion optics for the different carbon isotopes. The machine background obtained from unprocessed graphite samples is 0.02 percent modern carbon (pMC) corresponding to an apparent age of about 69.400 years.

The conversion of raw samples to sputter targets suitable for an efficient formation of negative carbon ions usually involves three steps. First, the samples are chemically pre-treated to remove carbon compounds which are not representative for the age, e.g. carbonates and humic acids in soil or conservation material in artefacts. Second, the remaining material with a typical carbon content of about 1 mg is oxidized to CO_2, which is performed at Erlangen in an elemental analyzer (EA), followed by a stable mass spectrometer for precision measurement of $\delta^{13}C$ from 1% of the CO_2. Third, CO_2 is catalytically reduced to carbon at high temperature. The use of an EA has the big advantage that both combustion and reduction are connected in a closed vacuum line with minimum contamination from outside and that both processes can be performed in a fully automated and time saving way. For a typical 1 mg sample the background from procession and machine is about 0.08 pMC corresponding to an apparent age of 57.300 years. To extend the range of applications beyond our standard samples (charcoal, soil, pollen, bones, mussels) attempts have been made for the radiocarbon dating of iron artefacts and lime mortar, which involves different pre-treatment techniques.

Some interesting archaeological applications of AMS will be shown, e.g. the ^{14}C dating of a “Persian mummy”. The application to geography is demonstrated by the investigation of wood samples from historic monasteries, temples and secular buildings in Tibet and Nepal. Here the ^{14}C measurements in combination with tree ring structure enable a highly resolved annual information about climatic variability in Tibet and the Himalayas in earlier times than that of the currently available dates. For applications concerning the biogenic or anthropogenic origin of environmental compounds (e.g. halogenated hydrocarbons in air rain or soil) the amount of carbon for radiocarbon measurements can be extremely low which makes an extension of the carbon mass range down to microgram highly desirable. To minimize any carbon contamination we have developed a closed system from gas chromatograph, used for fraction separation, via EA and a fully automatic gas handling system to the sputter ion source. With this new method modern and old calibration samples of ethyl alcohol with carbon masses down to 10 µg have been measured with reasonable results.

RADIOCARBON AGE OF *MIIDERA-GIRE* ATTRIBUTED TO *ENCHIN* AND THE HISTORICAL AGE IN WHICH AN ANCIENT MANUSCRIPT OF *MONZEN* WAS WRITTEN

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It is rare for ancient manuscript written in *Nara*, *Heian* and *Kamakura* periods (8-14th centuries) to be discovered as a complete book. *Kohitsugire* are ancient paper sheets containing elegant calligraphy. They were originally the pages of the ancient manuscripts; therefore, they constitute a vital resource for literature, history, and paleography. However, among the *kohitsugire* attributed to famous calligraphists, many copies and counterfeits written in several centuries later are in circulation. *Miidera-gire* is also well-known *kohitsugire* attributed to *Enchin* (AD814-891). It is a paper fragment of a Buddhist scripture written in a cursive hand. Among paleographers, it is commonly accepted that the cursive scripture was written in the early *Heian* period (roughly corresponding to 9-10th centuries).

The other side of this *kohitsugire* sheet has Chinese characters written in block script. It is a fragment of a book entitled *Monzen*, a collection of Chinese writing and poetry, hardly any ancient manuscripts of which are also remain. The paleographical style of the *Monzen* side seemed to be older than that of the Buddhist scripture and similar to the following Chinese manuscripts written in Tang dynasty (AD618-907): *Ohbotsu-shu*, *Kegonkyo*, *Sesetsusingo*, etc. We, therefore, measured radiocarbon age of the *kohitsugire* by accelerator mass spectrometry. The calibrated radiocarbon age indicated 671-778[cal AD] (2-sigma). It means that this *kohitsugire* was written in *Nara* period (AD710-794).

According to the radiocarbon dating and paleographical investigation, the *Monzen* was written first on the obverse side, and then, about one century later, the Buddhist scripture attributed to *Enchin* was written on the reverse side. Since only a few incomplete books written in *Heian* and *Kamakura* periods remain, this *kohitsigire* is one of the oldest examples among the extant manuscripts of *Monzen* in Japan. The old manuscripts are more valuable resources, because literals, missing and unnecessary letters, and malicious falsification increase as copying manuscripts are repeated. This *kohitsugire* has 45 words which can not be found in any another manuscripts. It seems that they were lost in copying. Several *kohitsugire* pages with identical handwriting sometimes discovered. They are called *tsure* and originally constituted a same book or series. Seven *tsure* of this *Miidera-gire* heve been already discovered. If more *tsure* can be collected, it leads to the reconstruction of the lost ancient manuscripts.

RADIOACTIVE EQUILIBRIA AND DISEQUILIBRIA OF U-SERIES NUCLIDES IN THE PRODUCTS FROM IZU ARC VOLCANOES, JAPAN

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The generation of arc magmas is generally inferred to be induced by the partial melting of the mantle wedge by the addition of fluid derived from the subducting plate.

The decay chain of ^{238}U ($t_{1/2}$ = 4.5 × 10^9 y) contains a number of radioactive intermediate nuclides with different chemical properties and half-lives. During magmatic processes from magma generation in the mantle wedge to the eruption, the differences in chemical properties between parent and daughter nuclides will allow them to be fractionated, generating radioactive disequilibrium. As the time since fractionation can be assessed using the half-lives of the daughter nuclides (*e.g.*, $t_{1/2}$ = 7.5 × 10^4 y for ^{230}Th, and $t_{1/2}$ = 1.6 × 10^3 y for ^{226}Ra), investigations of radioactive disequilibria among U-series nuclides in volcanic rocks can potentially provide informations on the time scale of magmatic processes. While the ^{238}U-$^{230\text{Th}}$ disequilibria can be used to estimate the time scale of an event of the U-Th fractionation within the period of 3.5 × 10^5 years (*i.e.*, 5 half-lives yield 97 % of the equilibrium), the ^{230}Th-^{226}Ra disequilibria can be used to estimate the time scale of an event of the Th-Ra fractionation within the period of 8.0 × 10^3 years. Radioactive disequilibria among ^{238}U-^{230}Th-^{226}Ra in the products from Izu arc volcanoes, Japan, were observed, in order to estimate the time scale of magmatic processes in Izu arc volcanism. Measurement of activity concentrations and activity ratios of U and Th isotopes in the volcanic products was made by isotope dilution analysis coupled with alpha-ray spectrometry. Ra-226 in the products was determined by gamma-ray spectrometry.

Activity ratios of ^{238}U/^{230}Th and ^{226}Ra/^{230}Th in the basaltic and andesitic products from Izu arc volcanoes were greater than unity, being enriched in ^{238}U and ^{226}Ra relative to ^{230}Th, which is often observed for volcanic products from young island-arc volcanoes. The ^{226}Ra/^{230}Th activity ratio versus ^{238}U/$^{230\text{Th}}$ activity ratio diagram for these products showed positive correlation, suggesting that the ^{238}U-^{230}Th-^{226}Ra disequilibria occurred during the magma genesis by the additions of U- and Ra-rich fluids derived from the subducting slab by dehydration to the mantle wedge. ^{238}U-^{230}Th-^{226}Ra radioactive disequilibria observed in the basaltic and andesitic products imply a short period of time (< 8000 years) between magma genesis and eruption.

The majority of rhyolitic products was considered to be almost in equilibrium of ^{238}U=^{230}Th=^{226}Ra. The observation that ^{238}U-^{230}Th-^{226}Ra for the rhyolite are in radioactive equilibrium suggested that the rhyolitic magma from Izu arc was generated in the partial melting of the crust, where ^{238}U-^{230}Th and ^{230}Th-^{226}Ra are in equilibrium, by the basaltic magma of high temperature.

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NUCLEAR FIELD SHIFT EFFECT IN ISOTOPE FRACTIONATION OF PALLADIUM USING A CROWN ETHER

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The classic theory of chemical isotope fractionation only predicts the mass-dependent isotope effect due to isotopic difference in vibrational energies of isotopologs [1]. Exceptions to the rule have been found since 1980s. Observed mass-independent isotope fractionations possessed a similar profile of the isotopic variation of their nuclear charge radii [2]. The conventional mass-dependent theory was reconsidered by one of the original authors, and the theory has been extended to include correction terms to account for nuclear properties, *i.e.*, nuclear mass, nuclear size and shape, and nuclear spin [3]. The nuclear field shift effect, which results from the isotopic change in the nuclear size and shape, is recognized as the major origin of the mass-independent isotope fractionation in chemical exchange reactions. The nuclear field shift effect is considered as a possible origin of isotopic anomalies found in several meteoritic samples [4-6]. The effect via chemical reactions may have accompanied the formation of these samples. In this context, it is important to demonstrate the mass-independent isotope fractionation by laboratory scale experiments with highly precise analytical methods.

Here, we studied the nuclear field shift effect of Pd. Palladium isotopes were fractionated by the liquid liquid extraction technique with a crown ether. After purification by ion-exchange chemistry, the isotopic ratios of ^{m}Pd/^{105}Pd (*m*: 106, 108, and 110) were measured precisely by multi-collector inductively coupled plasma spectrometry (MC-ICP-MS) at the "Pole Spectrometry Ocean" (PSO) of Brest. Isotope fractionations >0.1‰ have been found. In addition, the isotope enrichment factor of the odd atomic mass isotope (^{105}Pd) showed a depletion comparing to the even atomic mass isotopes (^{106}Pd, ^{108}Pd, and ^{110}Pd). In other words, the isotope enrichment factors of ^{106}Pd, ^{108}Pd, and ^{110}Pd showed a linear relation to their masses, while that of ^{105}Pd was smaller than a value estimated from the mass-dependent relation. The root mean square nuclear charge radius, $<r^2>^{1/2}$, of Pd isotopes increases with mass number [7]. $<r^2>^{1/2}$'s of ^{106}Pd, ^{108}Pd, and ^{110}Pd seem to increase linearly with the mass, while that of ^{105}Pd is smaller than a value expected by the relation. Hence, the odd-even staggering property found in the Pd isotope fractionation should originate from the nuclear field shift effect. Finally, the quantum chemical calculations for the different Pd species were realized to check the validity of the isotope enrichment factors obtained.

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ORBITAL PLANETARY GAMMA RAY SPECTROSCOPY: FROM CONCEPT TO SUCCESS

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Passive remote sensing of planetary surfaces using the lowest wave lengths developed from early concepts into an advanced nuclear analytical technique over the past fifty years. With successful completion of the Mars Odyssey Gamma Ray Spectrometry experiment late in 2009, this modality of planetary reconnaissance is celebrating a milestone of achievement in planetary exploration. As a result of this work, detailed maps of key element concentrations of the Martian surface now provide a valuable resource for interpretation for geo- and planetary scientists.

Early gamma ray experiments were flown on the American Ranger and the Russian Luna 10 missions. Gamma ray spectrometers measuring elemental composition from orbit flew around the Moon with the Apollo 15 and 16 missions, followed by other missions to the Moon, Mars and other planetary bodies culminating in the Mars Odyssey Mission. The presentation will comprehensively look at the technical and scientific development of orbital gamma ray spectrometry as a planetary exploration modality from its beginnings. Parallel to its scientific advancement, logic, and results it will provide for a description and analysis of the influence of science policy on the final establishment and success of planetary gamma ray spectrometry.

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INTERACTION OF URANIUM(VI) TOWARDS GLUTATHIONE – AN EXAMPLE TO STUDY DIFFERENT FUNCTIONAL GROUPS IN ONE MOLECULE

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Glutathione is a ubiquitous compound in living systems. It is a tripeptide containing besides two carboxylic groups also a thiol group as well as amino groups. Glutathione has antioxidant properties and therefore it helps to protect cells against reactive oxygen species. In plant cells glutathione is essential for the stress management.

Due to its carboxyl groups and the thiol group the peptide may contribute to the metal complexation. We have studied the complex behavior towards uranium(VI) exploiting several spectroscopic techniques, like UV-Vis and fluorescence measurements /1/. Direct UV-Vis measurements of the absorption spectra of the uranylspecies lead to a stability constant of log β121 = 38.70 ± 0.15. The glutathione itself does not absorb any light in the spectral range from 350 nm to 500 nm. Additionally the glutathione can be modified by fluoropyrovate in order to generate a species absorbing light in the wavelength range around 300 nm. The pyruvate group substitutes the proton of the thiol group. From these measurements a stability constant for the uranyl-glutathione complex was assigned to be log β121 = 38.85 ± 0.08.

Secondly we exploited the fluorescence properties of the uranyl ion. At a pH of 7.4 the main uranium species in carbonate free solutions are the hydroxospecies $(UO_2)_3(OH)_5^+$ and $(UO_2)_4(OH)_7^+$. By increasing the concentration of glutathione the fluorescence of these species disappears as consequence of the formation of a uranyl-glutathione complex. The stability constant using the Stern-Volmer equation was derived to be log β121 = 38.65 ± 0.02. Glutathione itself doesn't show any florescence properties. However, it is known, that the derivatisation of the thiol group by monobrombimane leads to a fluorescent glutathione species. In analogy to the measurements of the fluorescence of the uranylspecies the fluorescence of this conjugate also disappears upon complex formation with heavy metal ions.

The resulting stability constant for the uranyl complex was derived to be log β121 = 38.96 ± 0.02 neglecting that the thiol group was modified.

Summarizing all studies the stability constant for formation of a 1:1 uranyl-glutathione complex can be assigned to be log β121 = 38.79 ± 0.15. As the stability constants the measurements of the pure and the modified glutathione agree very well, w can conclude that the thiol group is not involved in the complex formation. Additionally it could be shown that glutathione does not reduce the uranium(VI) under the experimental conditions.

Comparing these data with stability constants for several flavonoids, showing also very high complex stability constants towards uranium, we conclude that glutathione in plant cells is much more involved in heavy metal stress reactions than flavonoids.

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GLUTATHIONE – A KEY FACTOR OF URANIUM TOLERANCE IN PLANT CELLS

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Uranium (U) is a widespread occurring radioactive toxic heavy metal. It could be accumulated in plant roots and to a lesser extent in leaves. Hence, it is mandatory for plants to develop sophisticated tolerance strategies against this heavy metal.

Glutathion is one of the key players in this network, because of its ability to complex heavy metals, its redox-capacity, and/or as precursor in the biosynthesis of heavy metal-binding peptides, e.g. phytochelatines. The cytoplasmic glutathione content (reduced glutathione, GSH) dropped on the half in cell suspensions of canola (*Brassica napus*) within the first 30 minutes after U contact. However, the GSH recovery to the normal level was reached after 60 minutes. Various U concentrations (1 – 50 µM) caused different GSH kinetics indicating several defence reactions.

Artificial depletion of cytoplasmic GSH with 1-chloro-2,4-dinitrobenzene (CDNB) enhances the U toxicity in cells determined by a metabolic test.

Because of a clear excess of GSH against the slowly accumulating U in the cytoplasm, the massive GSH decrease could not exclusively be dedicated to a complex formation between GSH and U. Additionally, a reduction of U(VI) to U(IV) can be ruled out because of a lack of U(IV) in cytoplasm revealed by photoacoustic measurements. However, the rapid GSH drop could be caused by its oxidation to GSSG (oxidized GSH). One possibility is the involvement of GSH in detoxification mechanisms against oxidative burst, e.g. reactive oxygen species (ROS), induced by U. Another could be the GSH dependent recovery of redox equivalents or other metabolites. Consequently, this GSH based detoxification processes will, at least transiently, generate a redox signal and therefore impact on cellular redox poise. It has to figure out weather the direct complexation of U with GSH (see abstract Geipel et al.) or the conjugation via glutathione S-transferase and the subsequent transport to the vacuole takes place. However, the formation of phytochelatines cannot be excluded because of cytoplasmic U bounded proteins being smaller than 14 KDa revealed by SDS gel electrophoresis and subsequent fluorescence measurements.

Further investigations should provide more detailed insights in the intracellular network of GSH functions in U detoxification as a redox buffer and as a detoxification reagent.

SEPARATION OF ^{60}Fe SAMPLES FROM AN IRRADIATED BEAM DUMP FOR NUCLEAR ASTROPHYSICS EXPERIMENTS

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Chemical separation techniques in liquid medium represent important requisites for special requirements in radiochemistry. In particular, when carrier-free (nca - so-called "non-carrier-added") radionuclides have to be handled, procedures carried out in aqueous solution are often the method of choice. The application fields are very broad, both for analytical and also preparative purposes. For instance, assembling of radiopharmaceutical drugs necessitates in any case an aqueous medium, and so do many other compounds for technological and scientific purposes. Another important scientific topic is the investigation of nuclear reactions with ^{60}Fe, ^{26}Al, ^{7}Be and others in nuclear astrophysics-related experiments. Highly enriched samples containing at least microgram amounts of the desired radionuclide are required for these studies. One of the very few possibilities for gaining such rare isotopes is the exploitation of activated components available from accelerator facilities at PSI. An initiative, called ERAWAST (Exotic Radionuclides from Accelerator Waste for Science and Technology) was created by the RadWasteAnalytics group at PSI aimed to develop separation strategies in a halftechnical scale for several interesting exotic radionuclides [1]. As an example, the preparation of two ^{60}Fe samples from an irradiated copper beam dump for nuclear astrophysics experiments is presented here.

The long-lived radionuclide ^{60}Fe plays a key role in nuclear astrophysics. Attempts at reconstructing the inventory of radioactivity between Fe and Pb require, among others, the exact knowledge of the half-life and experiments aimed to determine the neutron capture cross section. In particular, the half-life of 60Fe influences different astrophysical investigations. Most prominent examples are the nucleosynthesis in the current Galaxy as observed through γ-rays, the history of the Early Solar System as observed through meteoritic inclusions and deposits of supernova ejecta on Earth as observed in ocean-crust material.

Two ^{60}Fe samples were prepared from the copper beam dump mentioned above using liquidliquid extraction, precipitation and ion exchange [2]. The first sample was evaporated on a graphite backing and used for the first determination of the neutron capture cross section at stellar energies [3]. The second one served as sample for the re-measurement of the half-life [4].

This new value differs significantly from the previous one [5]. The two experiments were successfully performed in 2007 and 2008.

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PENNING TRAP EXPERIMENTS ON THE MOST EXOTIC NUCLEI ON EARTH: MASS MEASUREMENTS OF HALO NUCLEI AT TITAN

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Nuclei with an extreme unbalanced ratio of protons-to-neurons are referred to as exotic. The most exotic ones ever found on Earth are the halo nuclei of helium and lithum with a ration of three time more neutrons than protons. Teetering on the edge of nuclear stability, the properties of these exotic halo nuclei have long been recognized as one of the most stringent tests of our understanding of the strong force and provide ideal tests candidates for advanced theory. Only recently has it become possible to carry out precision mass measurement of the halos, such as 11Li, using a Penning trap spectrometer. Measurements were carried out at the TITAN (Triumf's Ion Trap for Atomic and Nuclear science) facility at TRIUMF where a trap system is coupled to the ISOL-based rare beam facility ISAC. Penning traps are proven to be the most precise device to make mass measurements, but were until now not able to reach these atoms, due to limitations in production yield and short half-lives. At TRIUMF we managed, and in addition to its unprecedented accuracy, $dm/m = 6\bullet10^{-8}$, the measurement of 11Li is remarkable for the fact that with a half-life of only 8.8 ms, it is the shortest-lived nuclide ever to be weighed with this technique. Furthermore, new and improved masses for 6,8He, and 11,12Be, hence precision mass measurements on 1,2, and 4-neutron halos have been performed. Using theses precision masses, other properties, such as charge radii form laser spectroscopy, can be derived. This allows one to test and refine state-of-the-art nuclear theory, and shows that three-body forces need to be considered when describing these nuclei. An overview of the TITAN mass measurement program and its impact in understanding halo nuclei will be given.

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FIRST DIRECT MASS MEASUREMENTS OF NOBELIUM ISOTOPES WITH SHIPTRAP

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Nuclear ground state properties represent key information on nuclear matter at the borderline of nuclear existence. The region of the superheavy elements that owe their stability to shell effects is of particular interest. In the last decades new elements up to $Z = 118$ have been synthesized on the route towards the next spherical shell closures above ^{208}Pb that are predicted around $Z \approx 120$ and $N \approx 184$. For a deeper understanding of the structure of superheavy elements accurate data on the properties of nuclides in the region $Z > 100$ such as half-lives, masses, and energies of excited states are crucial. These nuclides are now accessible for high-precision mass measurements with the Penning trap mass spectrometer SHIPTRAP at GSI. In 2008, the first direct high-precision mass measurements of the nobelium isotopes $^{252-254}$No ($Z = 102$) produced in the reaction $^{48}\mathrm{Ca}(^{206-208}\mathrm{Pb},2n)^{252-254}\mathrm{No}$ have been performed. The experiments were very challenging due to the low production rates. In the case of ^{252}No less than one ion per second was entering the SHIPTRAP stopping cell. These experiments are the first direct mass measurements in the region above uranium. The new, directly measured nobelium masses provide accurate reference points in this mass region and by α-decay links accurately determine the masses of heavier nuclides up to Ds ($Z = 110$). The experiments have paved the way for high-precision experiments on transactinides at low energy. In combination with laser spectroscopy and trap-assisted decay spectroscopy new accurate data on ground state properties of transactinides are now in reach.

ISOMER SPECTROSCOPY OF THE HEAVIEST ELEMENTS

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The specific “magic” proton and neutron numbers, representing major spherical shell gaps, beyond ^{208}Pb are a matter of considerable debate. It is well established that nuclei near Z=100, N=152 (^{252}Fm) have well-deformed prolate shapes. Orbitals that originate from above the predicted spherical shell gaps can intrude close to the Fermi surface of these deformed nuclei. There are also many high-K orbitals, which lie close to both the proton and neutron Fermi surfaces. This favors the occurrence of high-K multiquasiparticle isomeric states at low excitation energy. By identifying such high-K states, and studying their decay to states with lower-K, we can learn about the single-particle structure, pairing correlations, and excitation modes in the heaviest nuclei.

Experiments were carried out at the 88-Inch Cyclotron of the Lawrence Berkeley National Laboratory and used the Berkeley Gas-filled Separator (BGS). New high-K isomeric states have been identified in ^{255}Lr (Z=103) and ^{256}Rf (Z=104), representing the highest odd-Z and even-Z nuclei to be studied in this manner, to date. Detailed gammaray and electron decay spectroscopy has been performed. Three isomeric states have been discovered in ^{256}Rf and their decay properties are strikingly different from the high-K states seen in the lighter N=152 isotones. Two three quasi-particle isomers have been identified in ^{255}Lr and their decay populates lower-lying rotational structures. The behavior of these rotational bands provides new information on single-particle assignments and pairing properties. A recent experiment on ^{254}No (Z=102) has allowed us to follow the decay pathway of a four quasi-particle high-K isomer as it passes through rotational bands based on lower-lying two-quasi-particle states. We have also identified isomers in the N=153 isotones, ^{255}No and ^{257}Rf. The implications of all these results will be discussed.

CHEMICAL INVESTIGATION OF Rf AND Db AT JAEA

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We present a study of fluoro complex formation of the transactinide elements, rutherfordium (Rf) and dubnium (Db), at JAEA. The nuclides ^{261}Rf and ^{262}Db were produced in the reactions ^{248}Cm(^{18}O, 5*n*) and ^{248}Cm(^{19}F, 5*n*), respectively, at the JAEA tandem accelerator. Ion-exchange behavior of Rf and Db together with their respective lighter homologues in HF/HNO_3 mixed solution has been investigated with the rapid ion-exchange separation apparatus AIDA. It has been found that fluoro complexation of Rf is significantly different from that of the homologues. A large difference in the adsorption behavior of Db and the homologue Ta on the anion-exchange resin has been also observed. In the anion-exchange experiments, distribution coefficients (K_d) of Rf and the homologues Zr and Hf were measured as a function of the nitrate ion concentration $[NO_3^-]$ at the constant fluoride ion concentration $[F^-] = 3 \times 10^{-3}$ M. From the log K_d vs. log $[NO_3^-]$ plot, we unequivocally determined the species of Rf on the binding sites of the resin as the hexafluoro complex $[RfF_6]^{2-}$. The homologues are also to be present as $[MF_6]^{2-}$ (M = Zr and Hf), while the absolute *K*d values of Rf are about two-orders of magnitude smaller than those of the homologues. In the log K_d against log $[F^-]$ relation, the result indicated that at $[NO_3^-] = 0.01$ M, the formation of $[MF_6]^{2-}$ for Zr and Hf occurs at $[F^-] \sim 10^{-5}$ M, while that of $[RfF_6]^{2-}$ starts at around 10^{-3} M. There was about two-orders of magnitude difference in the fluoride ion concentration between Rf and the homologues for the formation of the hexafluoro complexes. This clearly demonstrates that the formation of the fluoro complexes of Rf is much weaker than those of the homologues Zr and Hf [1].

Cation-exchange behavior of Rf and the homologues in HF/0.1 M HNO_3 was also studied with the same manner as those in the anion-exchange experiments. The K_d values of Rf on the resin decreased with increasing $[F^-]$ in the range of 5×10^{-5} - 3×10^{-4} M due to the consecutive formation of fluoro complexes, while for the homologues the decreasing features of K_d were observed at about one-order of magnitude lower $[F^-]$ [2]. These results indicate that the transition from cationic to neutral and then anionic fluoro complexes of the group-4 elements requires higher $[F^-]$ for Rf than that for the homologues. The present result establishes the following sequence of the strength of fluoro complex formation, Zr ~ Hf > Rf that is the definite confirmation of the previously obtained results in HF solution [3, 4].

The anion-exchange experiment with Db has been conducted in HF/HNO_3 solution with the newly developed apparatus AIDA-II based on the model experiments with the homologues Nb, Ta and Pa. The result indicates that the adsorption of Db on the anion-exchange resin is quite different from that of the homologue Ta, while that is close to the adsorption of Nb and the pseudo-homologue Pa [5].

The present study at JAEA has been carried out in collaboration with RIKEN, Niigata University, Osaka University, Tokyo Metropolitan University, Kanazawa University, University of Tsukuba, GSI Helmholzzentrum für Schwerionenforschung, and Mainz University.

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RECENT UPDATES IN HEAVY ELEMENT PRODUCTION FROM LLNL

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The heavy element group at Lawrence Livermore National Laboratory (LLNL) has had a long tradition of nuclear and radiochemistry dating back to the 1950's. Some of the most exciting work has taken place in the last decade (in collaboration with the Flerov Laboratory of Nuclear Reactions in Dubna, Russia) with the discovery of five new elements - 113, 114, 115, 116, and 118. By pushing the boundaries of the periodic table, we can start to answer some of the most fundamental questions of nuclear science, such as the locations of the next "magic numbers" of protons and neutrons, and the possibility of an "Island of Stability" where nuclides would have lifetimes much longer than those currently observed in the heaviest elements. We have already seen evidence of extra-stability in the heaviest nuclides, which leads to half lives that are long enough for us to perform chemistry on these isotopes one atom at a time. In this presentation, recent results of heavy element experiments will be given.

THE CHALLENGE OF USING A PHYSICAL PRESEPARATOR IN CHEMICAL EXPERIMENTS WITH SUPER HEAVY ELEMENTS: THE STOPPING FORCE PROBLEM

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The irradiation of actinide targets with intense beams of ^{48}Ca is so far the most successful way to produce the super heaviest elements (SHE's, $Z \geq 112$) in nuclear fusion reactions, for review see [1]. Currently, chemistry experiments with SHE's formed in such reactions are performed with the gas-jet technique where most reaction products are collected in a gas thermalization chamber connected with the target assembly. The thermalized ions are transported to the experimental setups either attached to aerosol particles admixed to the carrier gas or – if they are volatile in their elemental state or as a formed volatile compound – in the pure carrier gas. This approach has the disadvantage that sophisticated systems are required providing high chemical separation factors to isolate and unambiguously identify single atoms of SHE's from the bulk of nuclear reaction by-products. The incorporation of a physical preseparation device between target and collection chamber opens up the perspective to perform much cleaner and partly novel chemical studies [2, 3]. Magnetic and electrostatic separators can be applied to physically separate the recoiling evaporation residues (EVR) via kinematic selection from vast amounts of by-products of the nuclear reaction [4-8] prior to entering a chemistry set-up. A gas catcher that stops the EVR's must be installed then in the ion optical focal plane of the separator. Due to the pressure difference between the gas-filled separator and the gas catcher, a physical detachment in form of a foil must be introduced. This foil has to be stable enough to withstand the applied pressure differences but also thin enough to efficiently let pass the low energy EVR's. Moreover, at a given size of the ion optical image of the target at the focal plane of the separator, the foil and the gas conditions in the catcher need to be adjusted to thermalize the EVR's in a gas volume kept as small as possible to provide a fast gas phase transport. Hence, such a combination of a physical preseparator and a chemical separation demands a detailed understanding of the stopping forces (STF) of the EVR's in solid and gaseous media.

In 2008 the first ever experiment to determine chemical properties of SHEs using a preseparator was conducted. Therefore, prerequisite measurements of the energy loss of mercury (Hg), radon (Rn) and nobelium (No) in Mylar and argon (Ar) were performed at low kinetic energies of around (40 – 270) keV per nucleon. The experimentally obtained values were compared with STF calculations of the commonly used program SRIM [9] in its actual version from 2008. The obtained data points have been used to extrapolate the STF of element 114, eka-lead, in the same stopping media. These estimations were applied to design a first chemical experiment with element 114 behind the Dubna Gas-filled Recoil Separator [7] at the Flerov Laboratory for Nuclear Reactions (Dubna, Russia) using the reaction ^{244}Pu(^{48}Ca;3n)^{289}114. One decay chain assigned to an atom of ^{285}112, the α-decay product of ^{289}114 was observed.

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EXTRACTION CHROMATOGRAPHIC STUDIES OF Rf AND Db HOMOLOGS

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Due to the short half-lives of the transactinide elements, fast and efficient separations are necessary so that the chemical properties of these can be studied and compared to those of their lighter homologs. Separations based on extraction chromatography resins show promise for achieving the required short separation times, high yields and high separation factors that are necessary for transactinide studies. Extraction systems that can be applied to the study of element 104, Rf and element 105, Db have been investigated. The adsorption of Zr and Hf, the lighter homologs of element 104, on different resins has been investigated from various acid matrices to evaluate the suitability of these systems for the study of Rf. Similarly, Nb and Ta have been used to assess the system for Db.

DECAY MODES AND A LIMIT OF EXISTENCE OF NUCLEI IN THE SUPERHEAVY MASS REGION

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Nucleus is a composite system consisting of protons and neutrons, and approximately 3000 nuclides have been identified experimentally. However, the existence of much more nuclides is postulated theoretically. How far the area of nuclei extends is an important question in nuclear physics.

We have developed an original model based on the macroscopic and mean-field models to describe the global feature of nuclear masses, called the KTUY (Koura-Tachibana-Uno-Yamada) nuclear mass model [1]. The standard deviation from known masses is 0.67 MeV, and below 0.4 MeV from some separation energies.

By using the KTUY model, we have studied decay modes for α-decay, β-decay, proton emission and spontaneous fission ranging from light nuclei to superheavy nuclei. In the previous work [2], we estimated dominant decay modes and discussed a possibility of existence of next "island of stability" in the region of superheeavy nuclei along neutron number N=228 in a considered region of N<250 due to the limit of calculation. After that work we extend the region of calculated nuclei to the much heavier region.

Figure 1 is a chart of estimated nuclear decay modes with longer lives than one nanosecond. In the heavier nuclear mass region, a large amount of nuclei placed over N=308 is shown. This is due to the strong magicity of N=308. The region of nuclei with longer lives than 1ns ends or is disconnected at N≈334. A solid curve as a fissility line is also drawn in the figure. This represents a macroscopic limit against spontaneous fission, and the curve and the neutron-drip line, which is shown as a comb-tooth shape here and determines the border in the neutron-side, is across each other at N≈334. Our calculation by using the KTUY model seems to be consistent with this macroscopic consideration. This calculation over Z>174 is not shown in the figure because of the limitation in our β-decay calculation. From the consideration of the macroscopic fissility line, however, the upper region seems to be not so extended or to be vanished quickly. We also calculate total half-lives. In this calculation we determined the number of nuclei depending on the half-life range. For example, the total number of nuclei with more than one nanosecond is estimated to be approximately eleven thousand. Some of other cases are shown in Table 1.

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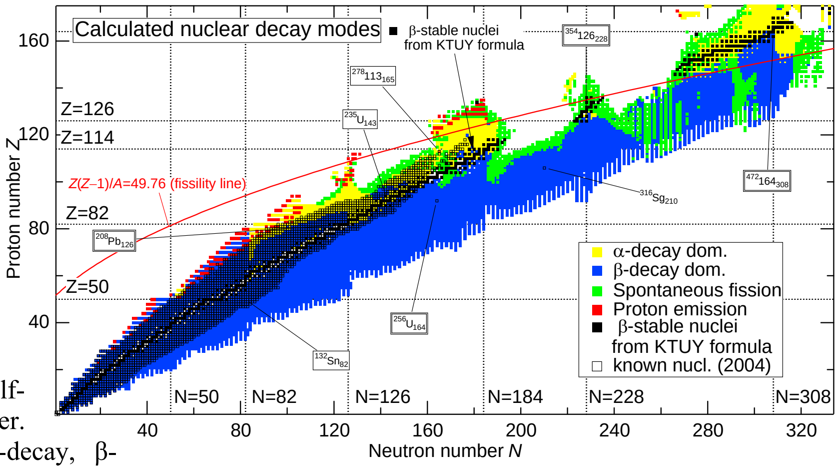

Fig. 1 Chart of the nuclides with half-lives of one nanosecond or longer. Dominant decay modes among α-decay, β-decay, proton emission and spontaneous fission are indicated.

Table 1. Number of nuclides with a certain half-lives or longer.

Shorter limit of half lives	1 s	1 ms	1 ms	1 ns
Number of nuclei	~4,000	~8,000	~10,000	~11,000

PRODUCTION AND DECAY PROPERTIES OF ^{266}Bh AND ^{262}Db BY USING THE ^{248}Cm(^{23}Na,5N) REACTION

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The identification of the heaviest nuclides is very difficult because of their extremely small production cross sections. A nuclide, ^{266}Bh, is the great-grand-daughter of ^{278}113 that is produced in the ^{209}Bi + ^{70}Zn reaction [1, 2]. The identification was based on a genetic link to the known daughter nucleus ^{266}Bh and ^{262}Db by alpha-decays. Only five atoms have been assigned to ^{266}Bh by direct production [3, 4]. In the present work, we produced ^{266}Bh in the ^{248}Cm + ^{23}Na reaction to obtain precise decay properties of ^{266}Bh and its daughter nuclides.

The experiment was performed at the RIKEN Linear Accelerator (RILAC) Facility. A ^{248}Cm$_2$O$_3$ target was prepared by electro-deposition onto a titanium backing foil. Six pieces of the target were mounted on a rotating wheel of a diameter of 10 cm. A ^{23}Na beam was extracted from RILAC. Beam energies of 126, 130, and 132 MeV were used. The ^{23}Na beam was pulsed with micro and macro pulse structures. The micro-pulse structure was used to prevent the irradiation of the target frame and the two vacant target positions of the wheel. In the macro-pulse structure, the beam was ON for 3 s and then OFF for 3 s independently of the micro-pulse structure. The typical beam intensity was 1 particle micro A on average, and the 1.9 x 10^{19} of beam dose was accumulated in about two months machine time. A gas filled recoil ion separator GARIS was used to collect evaporation residues and separate them from the beam particles. Silicon detector box was installed in the focal plane of GARIS. The total counting rate of the focal plane detector was approximately 3 x 10^4 /s in the beam ON period, while that was 5-10 /s in the beam OFF period. We have observed 32 correlations in total. 14 correlation events were clearly assigned to the decay chain of ^{266}Bh, and 10 correlations events were tentatively assigned to the decay chain of ^{266}Bh.

As a present result [5], a state in ^{266}Bh, which decays by an alpha emission with the energies ranging from 9.05 to 9.23 MeV, feeds a state in ^{262}Db, which decays by alpha emission and by SF with a previously known half-life. The result provided a further confirmation of the production and identification of the isotope of the 113th element, ^{278}113, studied by a research group at RIKEN. The isotope ^{267}Bh, which is a reaction product of the 4n evaporation channel, was also produced and identified. In this presentation, we will report the result of decay properties of ^{266}Bh and its daughter nuclei in detail.

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SYSTEMATIC STUDIES OF NUCLEAR FUSION REACTIONS AT LOW EXCITATION ENERGIES WITH ^{208}Pb TARGETS AND PAIRS OF PROJECTILES DIFFERING BY TWO NEUTRONS

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Elements 107- 112 [1,2] have been discovered in reactions between ^{208}Pb or ^{209}Bi targets and projectiles ranging from ^{54}Cr through ^{70}Zn. In such reactions, the compound nucleus can be formed at excitation energies as low as ~12 MeV, thus this type of reaction has been referred to as "cold fusion." The study of cold fusion reactions is an indispensable approach to gaining a better understanding of heavy element formation and decay. A theoretical model that successfully predicts not only the magnitudes of cold fusion cross sections, but also the shapes of excitation functions and the cross section ratios between various reaction pairs was recently developed by Świątecki, Siwek-Wilczyńska, and Wilczyński [3,4]. This theoretical model, also referred to as *Fusion by Diffusion,* has been the guide in our cold fusion studies.
To test and extend this model, four fusion-evaporation reactions were studied at the 88-Inch Cyclotron and the Berkeley Gas-Filled Separator at the Lawrence Berkeley National Laboratory: ^{208}Pb(^{48}Ti, xn)$^{256\text{-x}}$Rf, ^{208}Pb(^{50}Ti, xn)$^{258\text{-x}}$Rf, ^{208}Pb(^{52}Cr, xn)$^{260\text{-x}}$Sg, and ^{208}Pb(^{56}Fe, n)^{263}Hs. The data from these reactions, in addition to data from another six reactions, have been used for a systematic study of the difference in cross sections among the pairs of reactions with projectiles differing by two neutrons. Full excitation functions were measured for the 1n and 2n exit channels of the rutherfordium reactions. A full 1n excitation function was measured in the seaborgium reaction, while only a partial 2n exit channel excitation function was measured. Finally, in the ^{208}Pb(^{56}Fe, n)^{263}Hs reaction, no excitation function was measured due to the low cross section and the data were obtained at only one energy.

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EVAPORATION RESIDUE CROSS SECTIONS IN ^{28}Si + ^{176}Yb REACTION

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In heavy ions induced nuclear fission, fusion hindrance manifests as anomalous fission fragment angular distribution, broadening of fission fragment mass distribution and suppressed evaporation residue (ER) cross sections. Significant fusion suppression was reported in the reactions ^{19}F + ^{197}Au and ^{30}Si + ^{176}W based on the measurement of ER cross section [1]. Fusion hindrance in these reactions was attributed to the lower entrance channel mass asymmetry (α) for these reactions compared to the Businaro-Gallone critical mass asymmetry (α_{BG}). However, fusion hindrance reported in these reactions was observed to be much higher as compared to that predicted by pre-equilibrium fission model [2], which explains contribution from non-compound nucleus fission in terms of entrance channel mass asymmetry. Fission fragment angular distributions in the reactions ^{19}F + ^{197}Au and ^{24}Mg + ^{192}Os have been observed to be consistent with the pre-equilibrium fission model [3, 4]. In order to understand these contradicting observations, it was planned to measure fission fragment angular distribution and ER cross section in the reactions ^{16}O + ^{188}Os and ^{28}Si + ^{176}Yb which lead to the same compound nucleus ^{204}Po. Results of measurement of fission fragment angular distribution in the reaction ^{16}O + ^{188}Os and ^{28}Si + ^{176}Yb have been reported earlier [5]. For both the systems, fission fragment angular distributions were observed to be consistent with the statistical model calculations. In the present paper, we report the results of the measurement of ER cross section in ^{16}O+^{188}Os and ^{28}Si + ^{176}Yb reaction. Electrodeposited targets of ^{176}Yb (on aluminium backing) were bombarded with ^{28}Si beam and that of ^{188}Os (on Ni-Cu backing) with ^{16}O beam from BARC-TIFR Pelletron-LINAC facility. The ERs were measured at 5 different energies in the range 145-156.5 MeV for ^{28}Si beam and four different energies in the range 84-99 MeV for ^{16}O beam. The evaporation residues were assayed by off-line gamma-ray spectrometry. The fusion cross sections were calculated using the statistical model. The parameters for statistical model calculations were optimized by matching the calculated cross sections with the ER cross section for ^{16}O + ^{188}Os system, where contribution from non-compound nucleus fission is expected to be negligible. These parameters were then used to calculate the fusion cross section for ^{28}Si + ^{176}Yb system. The experimental ER cross sections were found to be lower as compared to the calculated fusion cross section values. This is consistent with the calculation of pre-equilibrium fission model which predicts about 10-20% fusion suppression in the reaction ^{28}Si + ^{176}Yb at the beam energies of the present study.

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INDIRECT DETERMINATION OF NEUTRON CAPTURE CROSS SECTIONS USING THE SURROGATE RATIO METHOD

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The Surrogate Ratio Method (SRM) has been developed as an indirect technique for the determination of neutron-induced reaction cross sections on both stable and radioactive nuclei, whereby surrogate reactions, using stable beams and targets, are used to populate the same compound systems as the neutroninduced reactions of interest. The relative decay probability for two different compound nuclei is measured and the unknown cross section is extracted relative to one that is well known. The recent extension of this method to the determination of neutron capture cross sections [1] suggests the SRM is a promising technique for obtaining nuclear data relevant for a number of applications, including advanced nuclear reactor performance calculations and the study of astrophysical phenomena. However, a deviation of the surrogate (n,*f*) cross section compared to directly measured data has been observed when two compound nuclei with dissimilar nuclear structure are compared in the SRM [2].
To explore the limits of applicability of the SRM in the determination of neutron capture cross sections, the effects of the nuclear structure of the two compound nuclei employed in the ratio was investigated. The relative γ-decay probabilities of the ^{162}Dy to ^{161}Dy and ^{162}Dy to ^{164}Dy residual nuclei, produced using light-ion induced direct reactions, were measured as a function of excitation energy using the CACTUS array at the Oslo Cyclotron Laboratory. The SRM was used to convert these relative γ-decay probabilities into the ^{161}Dy(n,γ) cross section in an equivalent neutron energy range of 130-560 keV [3]. The directly measured ^{161}Dy(n,γ) cross section, obtained from the Evaluated Nuclear Data Files (ENDF/B-VII), was compared to the experimentally determined surrogate ^{161}Dy(n,γ) cross section obtained using both similar (^{162}Dy to ^{164}Dy) and dissimilar (^{162}Dy to ^{161}Dy) compound nuclei pairs. The desired characteristics of the two compound nuclei employed in the ratio are demonstrated and a methodology for overcoming the limitations of the technique is suggested.

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HALF-LIFE MEASUREMENT OF ^{7}Be IN BUCKYBALLS AND HOST METALS

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As first suggested by Segr'e *et al.*[1], the electron-capture (EC) decay rate depends on the density of atomic electrons within the nucleus. Environmental factors such as chemical forms and pressure etc. may alter the electron contact densities in the nucleus and thus affect the electroncapture decay rates. The nucleus of ^{7}Be is a good candidate in which to look for such variations in environmental factors because of its simple electronic structure, $1s^22s^2$, in the EC decay nucleus. The ^{7}Be decays with a branching of 10.4% to a first excited state of ^{7}Li($1/2^-$ at 478 keV), which goes by γ emission to the ground state. Experiments to determine the decay rate of ^{7}Be in various environments, as a function of different chemical forms, host materials and under high pressure, have been investigated by several groups, and the differences found to be limited almost to within 0.2%. So far, the success of the ^{7}Be endohedral C_{60} ^{7}Be@C_{70} has allowed us to measure the half-life of ^{7}Be inside C_{60}[2,3]. In recent studies, large variations have also been observed in the sample of ^{7}Be@C_{60}[4,5], ^{7}Be@C_{70} and beryllium host metal as a function of temperature.

For example, the two samples, ^{7}Be@C_{70} (fastened in sample holder of the cryostat (5K)) and Be metal (^{7}Be) (293K), were placed in a computer-controlled sample changer, which precisely moved the samples in front of a HPGe γ-ray detector. The measurement was started after the ^{7}Be@C_{70} sample underwent sufficient cooling at T=5K under vacuum. The 478 keV γ-rays emanating from the EC-decay daughter of ^{7}Be were measured using a HPGe detector coupled to a 4096-channel pulse-height analyzer. The amount of radioactivity associated with the decay of ^{7}Be (Eγ=478 keV) could be uniquely analyzed through the identification of the γ-rays. The decay curves obtained in the present measurements were fitted, by use of the MINUIT program. Results of the half-life of ^{7}Be in the ^{7}Be@C_{70} and ^{7}Be@beyllium metal at T=5K and T=293K are compared and discussed in the conference.

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THE FUSION OF ^{9}LI WITH ^{208}PB

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We have measured the fusion excitation function for the ^{9}Li + ^{208}Pb reaction for near barrier ^{9}Li center of mass energies of 23.9 to 43.0 MeV using the ISAC2 facility at TRIUMF. The α-emitting evaporation residues ($^{211-214}$At) were stopped in the ^{208}Pb target and their decay was measured. The isotopic yields at each energy were in good agreement with the predictions of a statistical model code (HIVAP). The measured fusion excitation function shows evidence for substantial sub-barrier fusion enhancement not predicted by current theoretical models. There is a suppression of the above barrier cross sections relative to these model predictions. The implications of this measurement for studying the fusion of ^{11}Li with ^{208}Pb are discussed.

13-PS12 14158

THE ROLE OF EMISSION MÖSSBAUER SPECTROSCOPY IN THE STUDY OF SOPHISTICATED MATERIALS

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Mössbauer spectroscopy is a valuable tool for studying local sites on a microscopic level. Emission Mössbauer spectroscopy (EMS) is about 300 times more sensitive than the traditional absorption mode. Therefore, a few tens of parts-per-million substitution of 57Co at the active site (like Cu or Mn), is necessary with minimal perturbation of the ?sensitively tuned? Sophisticated material. 57Co acts as a nanoprobe and faithfully senses the subtle changes in the electron density, local dynamics, chemical environment, and magnetic behavior. For illustration, a few examples of our studies which led to a better understanding of superconductors and materials exhibiting colossal magnetoresistivity (CMR) will be discussed. EMS can also be used to great advantage for study of dynamics of molecules of biological interest like hemoglobin and vitamin B12.

13-PS10 22404

NEW STRATEGIES FOR THE DISCOVERY, PRODUCTION AND TRANSLATION OF NOVEL MOLECULAR IMAGING PROBES

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Modern radiopharmaceutical research largely focuses on finding ways to get medical isotopes to seek out specific biological targets associated with an injury or a disease state. This is done largely by radiolabeling a targeting vector in a manner that does not alter the parent compounds ability to seek out its target. The process of discovering molecular imaging probes that have high affinity for the target, sufficient stability in vivo while not binding to non-target tissue is exceptionally challenging. Finding clinically relevant compounds is made that much more difficult in that following the discovery of a viable lead agent robust production methods which meet strict regulatory standards must also be developed.

Researchers including our group are working on new technologies to expedite the discovery phase and to create production methods that are specifically designed for use with molecular imaging probes (as opposed to traditional perfusion based agents). This includes the use of automated discovery and labeling platforms, dual purpose probes and the creation of a new generation of instant labeling kits. The presentation will highlight the challenges and opportunities associated with the development of molecularly targeted radiopharmaceuticals and specific technological advances and will cover a range of medical isotopes including radiometals and radiohalogens. Additional information on initiatives in Canada to foster clinical translation and commercialization of novel agents will also be discussed.

PRODUCTION AND USE OF TIN-117m FOR APPLICATION TO THERAPY OF CANCER IN BONE

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As opposed to the many beta-emitters that are commonly used for therapeutic applications, tin-117m ($T_{1/2}$ 14.0) emits low-energy conversion electrons that deposit their intense energy within a very short range to destroy the tumor but not damage bone marrow or other normal tissues. In a pilot study in humans, tin 117m (4+) DTPA targeted bone with high affinity and, in cancer patients with bone metastases, ~70% of the injected dose localized and remained in the diseased bone. It delivered a concentrated radiation dose to bone metastases, with minimal bone marrow toxicity. Tin-117m DTPA is easy to prepare and is very stable (can be used for 2 months). The gamma photon (159 KeV; 86%) is ideal for imaging to monitor the cancer. The pain relief is long lasting and treatment can be repeated if necessary. Tin-117m DTPA has an overall excellent safety profile. Using this compound, a Phase I/II clinical trial involving 52 cancer patients showed total or very significant relief of pain in about 80% of cases (Srivastava et al., *Clinical Cancer Research* 4: 61-68, 1998). Pain relief was experienced within a week following a single dose of tin-117m DTPA, lasted for months up to over a year, and produced no side effects.

An extended Phase II/III clinical trial in an FDA-approved nationwide clinical trial in prostate cancer patients and patients with other cancers was also carried out. This trial aimed to compare tin-117m DTPA with *Metastron*, a radiopharmaceutical already approved to treat bone cancer pain. Patients receiving tin 117m DTPA received one of three doses, either one of the two amounts used in the previous BNL studies, or a higher dose. Patients receiving Metastron received the approved therapeutic dose of 4 mCi. Results in 72 prostate and 5 breast cancer patients showed >75% of the patients responding with substantial (>50%) or complete pain relief lasting for weeks to months or longer following a single administration. The main adverse effect of this treatment, transient myelotoxicity, was much less with the tin-117m therapy compared to other currently used bone pain palliation agents.

Our earlier pilot studies were carried out using low specific activity (5 – 20 mCi/mg) reactorproduced tin-117m from the $^{117}Sn(n,n'\gamma)^{117m}Sn$ reaction in the high fast neutron flux reactors at BNL and ORNL. For the clinical trials, higher specific activity tin-117m (~20mCi/mg) was produced at the SM-3 reactor in Dimitrovgrad, Russia.

More recently, we have developed the production of no-carrier-added (NCA) Sn-117m by highenergy proton irradiation (initial energy 160 MeV) of natural Sb providing a product with specific activity >1300 Ci/ g (Ermolaev et al, J. Radioanalyt. Nucl. Chem. 280; 319, 2009).To reduce the amount of tin-113 impurity in this material, we have explored the lower energy production method using enriched Sb-121 or Sb-123 targets. The results show that it is feasible to produce pure Sn-117m at lower proton energy with the following production yields: 4.8 μCi/μA·h at 30 MeV from ^{nat}Sb; 7.0 μCi/μA·h at 30 MeV from ^{121}Sb; 29μCi/μA·h at 55 MeV from ^{nat}Sb; 47 μCi/μA·h at 55 MeV from ^{123}Sb; and 79 μCi/μA·h at 72 MeV from ^{123}Sb. For better heat dissipation, a new target based on intermetallic compound TiSb has also been developed as well as solution chemistry to recover pure Sn-117m. This approach would thus allow widespread availability of high-purity NCA Sn-117m for various other therapeutic applications.

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ENERGY-EFFICIENT, ACCELERATOR-DRIVEN PRODUCTION OF ^{99}MO

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A concept for energy-efficient, large-scale production of ^{99}Mo and other useful short-lived fission products using low-enrichment uranium has been developed. The concept, a Compact Accelerator-driven Multiplier for Isotopes (CAMI), uses a small, nearly spherical array of low-enrichment uranium that contains a minimal quantity of ^{235}U at 19.9% of the total uranium mass. The CAMI is irradiated with neutrons generated by irradiation of an external target with a beam from an accelerator, with initial simulations assuming 200-MeV protons with ~100 kW beam power. The multiplication of this subcritical array is such that the beam power of 100 kW produces 1.2 MW of fission power resulting in a high yield of ^{99}Mo per gram of ^{235}U. The simulations indicate that 100% of the current U.S. demand of 40,000 Ci per week of ^{99}Mo can be delivered by this configuration. This production mechanism can provide a reliable domestic supply of ^{99}Mo using well understood technology and do so without the use of highly enriched uranium. Two other accelerator-based production mechanisms are currently being investigated, one based on photo-fission of ^{238}U, and the other based on the photo-nuclear reaction (gamma,n) on the stable isotope ^{100}Mo. Because these reactions require very high beam power they are limited to providing a relatively small fraction of the weekly supply of ^{99}Mo.

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14-TS12-1 16389

POSITRON STUDIES OF POLYMER THIN FILMS

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Polymer thin films feature prominently in vital technologies such as membrane-based separations, controlled storage and release matrices, opto-electronic devices, and sensors, and they take the form of coatings on substrate or free standing films or layers. The desired properties of these thin films include controlled mass transport properties such as permeability and selectivity.

Small molecule and ion diffusion through free volume elements in soft organic films is an inherently subnano or nanoscopic phenomenon [1]. Within polymer films free volume elements typically have a wide range of sizes and shapes and can exist as isolated pores, interconnected channels, or co-continuous or percolated structures. These free volume elements comprise a polymer film's ability to perform molecular separations or other diffusion dominated processes such as controlled release and physical ageing.

The ability to measure free volume elements in thin polymer films, ranging in film thickness from 50 nm to 500 nm, allows us to examine some of the polymer physics at the nanoscale, such as physical ageing and phase separation phenomena, which are dependent on or reflected by the free volume distribution.

This talk will survey current research trends in polymer thin films and present recent results in this field from our research.

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STUDY OF POLYMERS BY POSITRON ANNIHILATION SPECTROSCOPY

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Nanometer sized free volume holes in a polymer can be probed by positron annihilation lifetime spectroscopy (PALS) as long as a favorable fraction of positrons form positronium (Ps), the hydrogen-like bound state between a positron and an electron. Ps is formed by a reaction between a positron and one of electrons, ionized and liberated from the polymer molecules by the positron itself, in the terminal positron spur. Ps formation thus competes with positron and electron scavenging by polar groups, so that the yield of Ps strongly depends on the chemical structure of the polymer. In Ps forming polymers spin-parallel *ortho*-positronium (*o*-Ps) is localized in a nanometer sized free volume in the amorphous region. It then undergoes pick-off annihilation with a lifetime characteristic for the size of the hole, where it is localized. In the first part of the presentation the mechanism of Ps formation is discussed based on experimental results obtained for polymers with different chemical structures. In the second part of the talk, PALS is applied to the study of free volume in polymers with favorable Ps formation. Emphasis is placed on the usefulness of PALS in the study of the gas permeation mechanism in the polymers, with reference to good correlations between the free volume probed by PALS and oxygen permeability.

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PHYSICAL AND CHEMICAL INDUCED SPIN CROSSOVER

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Spin crossover is a kind of molecular magnetism, where switching between high spin (HS) and low spin (LS) states of a transition metal complex can be induced physically (e.g. by varying the temperature, or applying pressure or light) or chemically (e.g. through solvate or pH-change). In view of the drastic changes in structural, magnetic and optical properties accompanying the spin state transition, such compounds are currently subject to vigorous exploration regarding technical applications (e.g. storage, sensor or diagnostics). In this research area, the Mössbauer effect is used as a very powerful microscopic tool to study the spin state of iron spin transition compounds.
A compilation of selected results will be presented [1-5] (see Figure 1). Among them are some physical Induced-Excited-Spin-State-Trapping effects, e.g. via Nuclear decay (NIESST[1]), via Light (LIESST[1]), in Strong-Field-compounds via Light (SF-LIESST[1, 2]), via SOft-X-ray (SOXIESST[1]), or via HArd-Xray (HAXIESST[3]). As well as some light effects under continuous irraditation, e.g. the Light-Induced-Thermal-Hysteresis (LITH[1]), or the Light-Perturbed-Thermal-Hysteresis (LiPTH[1, 4]). Beside some chemical induced examples, e.g. hemoglobine, or molecular hygrometer[5]. In multinuclear compounds the switching follows an concerted or sequential mechanism[1].

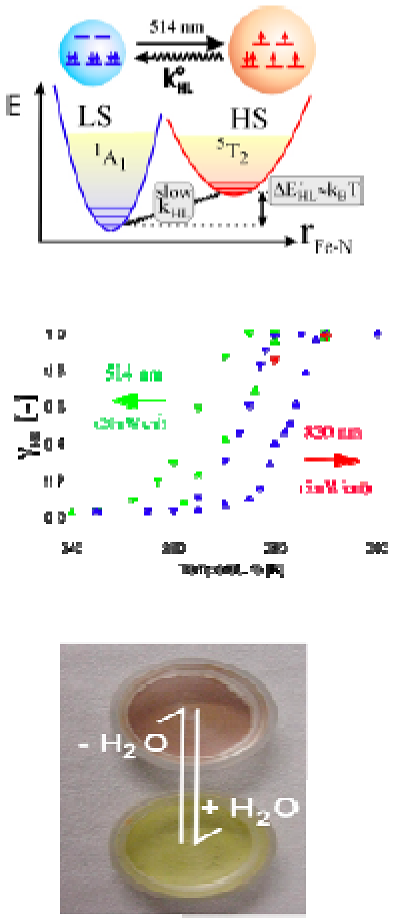

Figure 1: (upper) LIESST and SF-LIESST[1, 2], (middle) LiPTH[1, 4], and (lower) the hygrometer[1, 5].

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CHARACTERIZAION OF ^{57}Fe IMPLANTED SnO_2 FILMS BY MöSSBAUER SPECTROSCOPY AND NUCLEAR INELASTIC SCATTERING

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The as implanted sample at room temperature and post-annealed samples did not show Kerr effect, but the sample implanted with $1x10^{17}$ Fe ions/cm^2, heated at 300^{o}C, showed a little Kerr effect although the magnetic sextets were not clearly observed in ^{57}Fe CEM spectra. The Kerr effect disappeared after post-annealing. This suggests that the number of magnetic defects decreases by absorption of oxygen [1]. We also showed that the bulk magnetization is enhanced by co-doping of Sb and Fe into SnO_2 powder [2]. We have analyzed the nanostructure of SnO_2 films doped with ^{57}Fe by conversion electron Mossbauer spectroscopy (CEMS) and nuclear inelastic scattering (NIS) at SPring8.

We implanted ^{57}Fe with $5x10^{16}$ ions/cm^2 into SnO_2 films containing 0.1% Sb and 3% Sb at the substrate temperature of 500^{o}C in vacuum. Kerr rotation angles for 0.1% Sb doped SnO_2 film were larger than that for 3%Sb doped SnO_2 films. The samples post-annealed at 400^{o}C for 6 hours also showed the Kerr effect. DCEM spectra were measured by discriminating conversion electrons with a back scattered type of gas counter [3]. As the results, four subspectra were observed: two doublets are assigned to paramagnetic Fe^{3+} and Fe^{2+} species and two broad sextets to site A and site B of magnetite. For 0.1%Sb doped SnO_2 films the relative area of the magnetite phase was larger than for 3%Sb doped SnO_2 films. After post-annealing, two sextets changed into one broad sextet, which is due to fine maghemite. The ferromagnetic behaviors of Fe implanted tin oxide films were attributed mainly due to the formation of magnetite for the as implanted samples and of maghemite for the post-annealed samples, respectively, rather than magnetic defects.

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^{57}Fe MÖSSBAUER SPECTROSCOPY WITH MIMOS II AT THE SURFACE OF MARS

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The NASA Mars Exploration Rovers (MER), Spirit and Opportunity, landed on the Red Planet in January 2004. Both rovers are equipped with a miniaturized Mössbauer spectrometer MIMOS II [1]. Designed for a three months mission, both rovers and both Mössbauer instruments are still working after more than five years of exploring the Martian surface. At the beginning, with a landed intensity of the MB source of 150 mCi, a 30 minute 'touch and go' measurement produced already valuable data while a good quality Mössbauer spectrum was obtained after approximately four to six hours. Now after more than six halflifes of the sources typical Mössbauer integrations last ~40 hours but are still of outstanding quality and scientific importance.

Summarizing important Mössbauer results, Spirit has traversed the plains from her landing site in Gusev crater and is now, for the greater part of the mission, investigating the stratigraphically younger Columbia Hills. Comparison of simultaneously acquired 14.4 keV γ-ray and 6.4 keV X-ray spectra provides depth sensitivity, and the average thickness of thin coatings on several basalt was estimated to approximately 10 μm [3]. Hematite and Goethite identified in rocks at the West Spur of the Columbia Hills are clear mineralogical evidence that water played a major role in the formation and alteration of rocks and soils in the Columbia Hills [4-5]. Home Plate is a layered plateau of probably explosive volcanic origin in the Inner Basin of the Columbia Hills [6]. Opportunity at Meridiani Planum travelled more than 17 km across sulfate-rich outcrop, basaltic sand and dust, and hematite lag deposits [2]. The ferric sulfate hydroxide mineral jarosite was identified in sulfate-rich outcrop rocks. Millimeter-sized spherules nicknamed Blueberries were identified as the source of hematite detected from orbit. Crater hopping from her landing site in ~ 20 m Eagle crater via ~ 160 m Endurance crater, 300 m Erebus crater to ~ 800 m Victoria, Opportunity was operating within Victoria crater the last few month in 2008, and is now proceeding towards 22km diameter crater Endeavour, about 12km to the southeast of Victoria. The primary MER objective was to explore two sites on the Martian surface where water may once have been present, and to assess past environmental conditions at those sites and their suitability for life. The MER Mössbauer spectrometers identified aqueous minerals such as goethite in Gusev crater and jarosite at Meridiani Planum. Jarosite forms under acidic conditions which would have challenged prebiotic chemical reactions [7].

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IMPROVEMENT OF SIGNAL-TO-NOISE RATIOS IN ^{57}Mn IMPANTATION MÖSSBAUER SPECTROSCOPY

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Recent remarkable developments of radioisotope beams have provided new applications to the scientific fields of nuclear physics, material science, and chemistry. We have studied unusual and exotic chemical states of ^{57}Fe created through β decays of short-lived ^{57}Mn nuclei ($T_{1/2}$= 1.45 min) implanted into $KMnO_4$ [1], graphite (HOPG), solid oxygen [2] and Si semiconductors [3], by means of ^{57}Mn emission Mössbauer spectroscopy. The ^{57}Mn dominantly decays to the 14 keV Mössbauer level of ^{57}Fe via a β -emission. In these experiments, a gas-filled resonant detector with a built-in ^{57}Fe-enriched stainless-steel absorber was used to obtain Mössbauer spectra. This detector, which is called a parallel-plate avalanche counter (PPAC) [4], possesses brilliantly a high sensitivity for the detection of 14 keV β rays by collecting the conversion electrons emitted from ^{57}Fe-enriched stainless-steel absorber by Mössbauer effect. However, there still remained a significant problem that the β -rays emitted from ^{57}Mn nuclei much degraded a signal-to-noise ratio (S/N) of the Mössbauer spectra because PPAC has poor energy resolution to discriminate the real conversion electrons from the incoming β rays. In the present work, our detection system was improved by using an anticoincidence method where a thin plastic scintillation counter was set between the PPAC and a sample in order to reject the β rays that induced high background, and we succeeded to obtain Mössbauer spectra of ^{57}Fe in a nonmagnetic metal Al with very large S/N.

The experiment was performed at Heavy Ion Medical Accelerator in Chiba (HIMAC) of National Institute of Radiological Sciences (NIRS). The ^{57}Mn beam was produced through the projectile fragmentation process with irradiations of ^{58}Fe ions accelerated at 500 MeV per nucleon on a Be target (27mm thick), and the intensity of 57Mn beam was around 106 pps. The 57Mn nuclei were implanted into an Al plate (50mm x 50 mm x 1mm thick) at room temperature after passing through Pb/Al/acrylic plates in order to stop all the nuclei at adequate depth in the Al sample. Immediately after the ^{57}Mn decayed to ^{57}Fe (~ 100 ns), the 14 keV γ rays emitted from ^{57}Fe were detected by the PPAC that was mounted on a Mössbauer transducer. As a result, it was found that the S/N of obtained Mössbauer spectrum with the anticoincidence method increased to be more than tenfold better than that of the previous ones without the electron rejection. We will introduce the experimental procedure and discuss the obtained results in detail.

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PRODUCTION OF Mo-99 AND Tc-99m VIA ALTERNATIVE ROUTES

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With the increasing problems with the ageing reactors that are the primary source for the Mo-99 used in Tc-99m generators alternative routes of production are being sought. The root of the difficulties with production and alternative means for production using accelerators will be explored.

15-S10-2 14616

ISOTOPE PRODUCTION FOR MEDICAL USAGE USING FAST NEUTRON REACTIONS

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^{99m}Tc is the most important radioisotope used as nuclear medicine. The present world demand for ^{99}Mo is about 450 TBq/week which is mostly produced by using only five nuclear reactors in Canada, Belgium, France, Netherlands and South Africa. In 2007, the unanticipated closure of a nuclear reactor in Canada for five weeks reinforced concerns about a reliable long-term supply of ^{99}Mo. Note that the reactors mentioned above range in age from 42 to 51 years. Also another problem is that 95-99 % of all ^{99}Mo is produced by the irradiation of highly enriched uranium targets. In order to guarantee safe and reliable supply of ^{99}Mo, IAEA recommends to use the ^{98}Mo(n,γ)^{99}Mo reaction.

Recently, two of the present authors proposed a new route to produce ^{99}Mo by the ^{100}Mo(*n,2n*)^{99}Mo reaction, which has the following characteristic features.1) First, the reaction cross section is large, about 1.5 barn at 12<En<17 MeV, which is 10 times larger than the thermal-neutron capture cross section of ^{98}Mo. Second, the cross sections of the (*n,*α), (*n,np*), and (*n,p*) reactions are less than a few mb at En = 14 MeV. Third, a large amount of ^{100}Mo target materials can be used, compared to that for proton beam irradiation on ^{100}Mo. Fourth, intense neutrons with energy of 12-17MeV are already available. In the present work we have measured all γ-rays emitted from activities produced by bombarding a natural Mo target with neutrons from the D(^{3}H,n)^{4}He reaction at Fusion Neutronics Source Facility (FNS) at Japan Atomic Energy Agency (JAEA) to study characteristic features mentioned above more in detail. The neutron flux was about 10^{12} n/cm^{2}s. The experimental results at FNS will be discussed in the conference.

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THEORETICAL ASSESSMENT OF SPECIFIC RADIOACTIVITY: THE EFFECT OF TARGET BURN-UP, ISOTOPE DILUTION AND TARGET PURITY AND THE APPLICATION FOR ^{177}LU PRODUCTION

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The wide expansion of targeting radiotherapy depends a lot on the availability of metallic radionuclide with high specific radioactivity (SA). As an example, as high as 20 Ci/mg SA of ^{177}Lu is required to formulate the targeting radiopharmaceuticals for different cancer treatments. High SA nuclide can be produced using a neutron capture reaction of the target nuclide of high cross section (such as ^{176}Lu (n, γ) ^{177}Lu, б = 2300 b). This direct route could be successfully performed in the nuclear reactor of rather high neutron flux which is accessible in only a handful of countries in the world. However, large burn-up of the target nuclide during high neutron flux irradiation may cause a problem of degrading the SA value of the produced nuclide if the target contains isotopic impurities. No-carrier- added (n.c.a) radioisotopes can be produced via a process of neutron capture-followed-by- β - decay (such as ^{176}Yb (n, γ) ^{177}Yb (β - decay) ^{177}Lu). In this case, the same reduction in isotope SA was also experienced if the target contains the isotopic and/or elemental impurities, one radionuclide of which is expected to be produced. The ^{177}Lu production was reported in many publications 1-3, but until now the product quality assessment, especially the evaluation of ^{177}Lu specific radioactivity in the product is not sufficiently performed. The SA assessment was based on the calculation of nuclear reaction and radioactive transformation yield as a function of thermal neutron flux, target nuclide burn-up, isotopic composition and irradiation and post-activation processing time.

Among the factors affecting SA the target composition (elemental and isotopic impurities), target nuclide burn-up and the irradiation and processing time are most accounted for. Theoretical SA assessment has definitely given us a firm ground to set up an optimized process for the production of clinically applicable radioactive product. The maximal radioactivity of R_i nuclide in the target ($A_{Ri-\max}$) achieved at the specified irradiation time $t_{irr(Ri-\max)}$ was calculated based on the following equations:

$$t_{irr(R_i-\max)} = \ln(\frac{\lambda_{R_i}}{\Delta_{X_1}})/(\lambda_{R_i} - \Delta_{X_1}); \qquad A_{Ri-\max} = N_{o,X_1}.\phi_{th}.\Omega_{i,X_1}.(e^{-a} - e^{-b})/c$$

The maximal SA value was also achievable but not at the irradiation time $t_{irr(Rf\text{-}max)}$. *The specific radioactivity of radionuclide Ri formed via neutron capture reaction and its application for ^{177}Lu production using ^{176}Lu (n, γ) ^{177}Lu reaction.* The ^{177}Lu specific radioactivity

$$SA_{R_1-t_{irr}-t_c} = 100\ /\{1 + \frac{(\lambda_{R_1} - \Delta_{X_1}).(M_2.P_{X_1}.e^{-\Delta_{X_1}.t_{irr}} + M_1.P_{X_2}.e^{-\Delta_{X_2}.t_{irr}})}{M_2.P_{X_1}.\phi_{th}.\Omega_{1,X_1}.(e^{-\Delta_{X_1}.t_{irr}} - e^{-\lambda_{R_1}.t_{irr}}).e^{-\lambda_{R_1}.t_c}}\}$$

^{177}Lu specific radioactivity as a function of target isotopic composition, neutron flux, irradiation time was formulated and calculated (Fig.1). The maximal values of 177Lu specific radioactivity was evaluated and used as optimal conditions for carrier contained ^{177}Lu production.

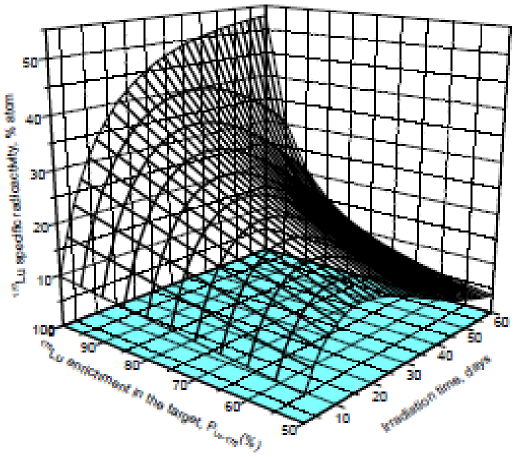

Fig. 1. ^{177}Lu specific radioactivity as a function of the irradiation time and ^{176}Lu isotopic purity in the target (Thermal neutron flux of 2.5×10^{14} n.cm^{-2}.s^{-1} was appli Nuclear data was extracted from literatures $^{4-5}$)

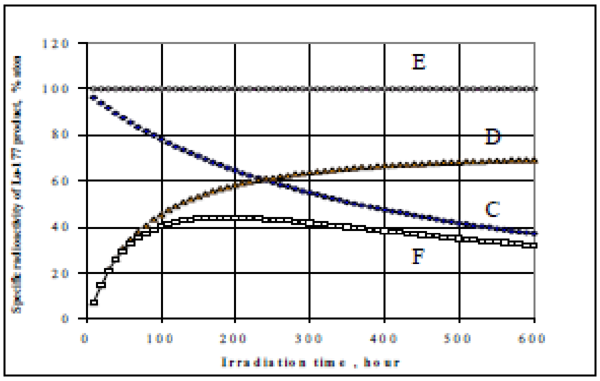

Fig. 2. SA of n.c.a ^{177}Lu in the ^{176} Yb target as a function of irradiation time and content of ^{174}Yb and elemental Lu impurities.
C: Specific radioactivity of ^{177}Lu isotope in the target containing 1.93% ^{174}Yb; **D:** Specific radioactivity of ^{177}Lu isotope in the target containing 50 p.p.m Lu impurities; **E:** Specific radioactivity of ^{177}Lu isotope in the impurity-free target; **F:** Specific radioactivity of ^{177}Lu isotope in the target containing 1.93% ^{174}Yb and 50 p.p.m Lu impurity.

The specific radioactivity of radionuclide Ri formed via neutron capture followed by radioactive transformation and its application for ^{177}Lu production using indirect route ^{176}Yb (n, γ) ^{177}Yb (β- decay) ^{177}Lu. In contrast to the direct route involving the ^{176}Lu (n, γ) ^{177}Lu reaction, the indirect production route of ^{177}Lu using ^{176}Yb enriched target gives a product of high SA. However, the product is never carrier free due to the elemental Lu and isotopic ^{174}Yb impurities in the ^{176}Yb enriched target. ^{175}Lu isotope generated from ^{174}Yb (n, γ) ^{175}Yb (β- decay) ^{175}Lu process and elemental Lu impurities remaining in the ^{177}Lu product (which is chemically separated from ^{176}Yb target) makes the ^{177}Lu SA value strongly decreased. Based on the above mentioned assessment method the effect of several factors (such as elemental Lu impurity, isotopic ^{174}Yb content and isotope dilution) on the ^{177}Lu SA degradation was evaluated. The specific radioactivity of n.c.a ^{177}Lu radioisotope produced by the ^{176}Yb (n, γ) ^{177}Yb (β- decay) ^{177}Lu process as a function of the elemental and isotopic impurities of the ^{176}Yb enriched target and the irradiation conditions is shown in Fig.2. As a result obtained, the specific radioactivity of n.c.a ^{177}Lu produced from ^{176}Yb target was strongly affected by irradiation time and impurities of the target. The production yield and desired specific activity should be compromised to achieve a cost effective production of clinically applicable ^{177}Lu product. The experimental results reported in our previous publications have well agreed with theoretical calculation results[3].

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TECHNETIUM BROMIDES: FUNDAMENTAL STUDIES AND ADVANCES TOWARDS THE SYNTHESIS OF LOW VALENT TECHNETIUM COMPLEXES

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Due it the radioactivity of all of its isotopes, technetium is the least understood d-block element. For example, the structure of TcO_2 was first reported in 2007, and only 3 Tc binary halides had been reported prior to this project, compared to 13 for Re. This talk presents our recent synthesis and characterization of technetium $TcBr_3$ and $TcBr_4$, the first simple halides of technetium to be reported in the past 40 years. In addition to the study of their fundamental properties, we have investigated the potential of these new binary bromides as precursors in the synthesis of new compounds. For example, when technetium tribromide was reacted with trimethylphosphine, the new Tc complexes, monomeric $TcBr_2(PMe_3)_4$ and dimeric $Tc_2Br_4(PMe_3)_4$ formed.

The above compounds were characterized by single crystal diffraction, UV-Visible spectroscopy and DFT calculations. $TcBr_2(PMe_3)_4$ is the first of the *trans*-dihalo-tetrakis-trialkylphosphine metallate class reported for group VII. The electronic structure of $TcBr_2(PMe_3)_4$ was investigated by DFT methods and will be described. Further calculations indicate that its rhenium homologue is stable and may be possible to prepare. The synthesis of $TcBr_2(PMe_3)_4$ clearly show the potential of technetium bromides to produce new compounds and it is our expectation that other interesting complexes will be produced.

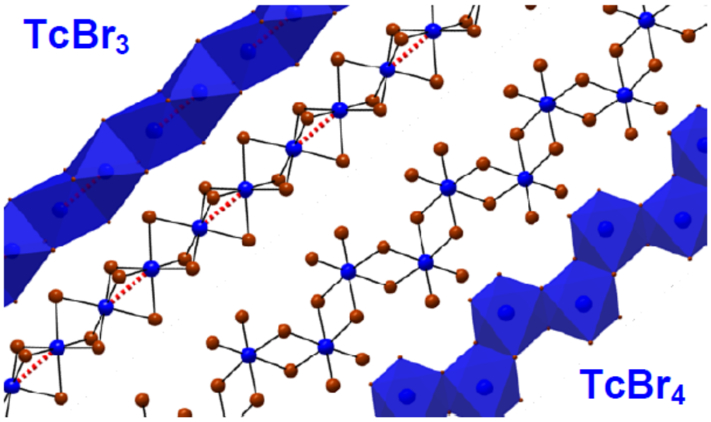

Figure 1: Structure of 1D technetium bromide chains from TcBr3 and TcBr4.

15-S10-5 20474

EVALUATION OF SCANDIUM-POLYAMINOPOLYCARBOXYLIC COMPLEXES AS A NEW GENERATION OF PET AGENT AND RADIOPHARMACEUTICAL

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Scandium isotopes (^{44}Sc and ^{47}Sc) are becoming more available due to development of generators. Their properties are convenient for both PET imaging or for radiotherapy. To use them in nuclear medicine, ligands forming complexes endowed with a high stability are necessary. However, complexation chemistry of trivalent scandium has not been studied well enough to suggest suitable ligands. Ligands of the polydentate aminopolycarboxylates such as DTPA, DOTA, NOTA or TETA, are initial choices since they form stable complexes with lanthanide(III) ions and with Y(III) belonging to the same column as Sc(III) of the periodic table. The determination of the thermodynamic stability constants of these ligands with Sc(III) is needed to determine which ligand is optimal.

Available experimental data on stability constants of complexones such as DTPA, DOTA, NOTA and TETA have been published for some time and are recognized as reference values. Scandium is the exception since no relevant data is available. For the first time, reasonable numerical values of stability constants of Sc(III) with H_3NOTA, H_4TETA, H_4DOTA and H_5DTPA were obtained by potentiometry, ^{1}H/^{45}Sc NMR and a displacement method.

The aim of this work is i) to determine the number and stoichiometry of the complexed species and ii) to report the stability constant values for Sc^{3+} with DOTA, DTPA, NOTA and TETA using potentiometry together with ^{1}H/^{45}Sc NMR measurements. In addition, a radiochemical displacement method was employed to determine the stability constants at the tracer level, using a cationic exchange resin. Finally, it is of benefit to screen metal complexes of radiopharmaceutical interest *in vitro*, to gauge qualitatively their potential *in vivo* stability and hence their suitability for further biological studies. In this work we also describe a series of *in vitro* assays to assess the potential *in vivo* stability of these potentially new radiopharmaceuticals.

EFFICIENT APPROACHES TO LABELING RADIOPHARMACUETICALS WITH FLUORINE-18

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There has been a steady increase in the number of fluorine containing biologically active molecules. There are a number of strategies that have been employed to incorporate fluorine-18 in candidate radiopharmaceuticals for positron emission tomography (PET) imaging. Fluorine-18, first discovered in 1936 at the Berkeley Radioation Laboratory, possesses favorable properties for synthesis and imaging. Production of fluorine-18 today for PET imaging involves the proton irradiation of enriched oxygen-18 water to produce [^{18}F]fluoride ion or irradiation of enriched oxygen-18 gas ([^{18}O]O_2) in the presence of fluorine-19 fluorine gas ([^{19}F]F_2) to give fluorine-18 fluorine gas (^{18}F-^{19}F; [^{18}F]F_2 gas). An alternative method exists to convert [^{18}F]fluoride ion to [^{18}F]F_2 gas through and electric discharge process. In an effort to speed the process of incorporation of fluoinre-18 into organic molecules two automated processes have been developed. The first process involves the introduction of fluorine-18 into the fluoromethane ([^{18}F]CH_3F) and aromatic rings without the need to completely dry the aqueous [^{18}F]fluoride ion from the cyclotron target. The second process involves the automated conversion of the [^{18}F]CH_3F into [^{18}F]F_2 gas. In the former process the aqueous [^{18}F]fluoride ion is trapped on ion exchange column and released in the desired reaction solution. Incorporation of [^{18}F]fluoride ion into the molecules is facilitated by conventional or microwave heating. In the latter process [^{18}F]CH_3F is electrolytically converted into [^{18}F]F_2 gas which is then used to label biologically active molecules. These approaches facilitate the efficient incorporation of fluorine-18 into useful imaging agents.

16-PS9 18420

APPLICATION OF RADIOISOTOPE MEASUREMENT FOR PLANT STUDY: FROM ACTIVATION ANALYSIS TO RADIOISOTOPE IMAGING

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Plants live on only water and 17 inorganic elements. Though the number of researches applying radio-analytical method to plants has been decreasing, there is a great advantage of this method. We present how radio-analytical tool reveals the new physiological activity of plants. First, water distribution was analyzed through neutron beam analysis and water uptake amount was measured using ^{15}O-labeled water, which half-life is only 2 min. We found that tremendous amount of water was always leaking out from xylem tissue and re-entered to the tissue, where xylem was regarded as a mere pipe to transport water. Next, tissue specific elemental distribution was analyzed through neutron activation analysis. There was an element specific distribution spread out throughout the plant tissue and this profile was kept the same throughout the developmental stage. To image and measure the real-time element uptake from roots, we developed RI imaging system, where any beta-ray emitters, except for ^{3}H, were visualized. Though there is an overwhelming development of imaging system using fluorescent dye or probes, unless using radioisotopes, it is impossible to image the elemental movement under light condition and numerical treatment of the image. The system we developed converts beta-rays emitted from the sample to light by a Cs(Tl)I scintillator and was guided to a highly sensitive CCD camera. Applying this system, it was shown that roots absorb phosphate indifferent to light or dark but the translocation of nutrients in leaves was highly dependent on light. It was also able to visualize the element uptake manner of the roots in the presence of soil.

16-PS2 21948

WHY NUCLEAR FORENSICS?

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The application of nuclear forensics to deal with the problems of nuclear proliferation and nuclear terrorism are at the intersection of science and policy. Compliance with international treaties, relations between nations or decisions to go to war sometimes rest on the outcome of forensic investigations. I will draw on some examples that caught international attention over the past two decades. Did North Korea reprocess more than the plutonium it declared in 1992? What was the origin of plutonium found in German and Czech cities in the mid-1990s? How far did Iraq get with its nuclear program before the Gulf War and how much continued? What was the origin of the uranium hexafluoride that Libya turned over to Americans? What were the origins of the highly enriched uranium particles recently found in Iran? Were the results of forensic studies on articles provided by North Korea consistent with its declaration of the nuclear program? I will discuss some of the questions that posed significant scientific challenges and elaborate on the diplomatic consequences of the investigations.

16-PS3 22364

MEASUREMENT OF NICKEL-63 FOR REASSESSMENT OF NEUTRON DOSIMETRY FOR THE HIROSHIMA ATOMIC BOMB

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The radiation effect on human health has been evaluated on the basis of the exposure dose of the atomic bomb survivors at Hiroshima and Nagasaki. In the Tentative 1965 Dose (T65D) [1], tissue doses were estimated by data obtained from atomic bomb tests and reactor simulation experiments. However, the dependence of the leukemia risk on dose was not consistent with Hiroshima and Nagasaki atomic bombs. In order to reevaluate the radiation doses, the Dosimetry System 1986 (DS86) [2] was established mainly by model calculations of neutron and gamma ray transport. Then, the measurements of residual radioactivities were performed to validate the calculated neutron doses of DS86. From the analysis of thermal neutron induced products of ^{60}Co ($T_{1/2}$ = 5.27 y) and ^{152}Eu (13.3 y) [3], it was suggested that the derived neutron spectrum for the Hiroshima atomic bomb is harder than that given in DS86. In order to solve the source of this discrepancy, the measurement of the fast neutron product was particularly desirable.

We developed the measurement method of the residual radioactivity of ^{63}Ni (100 y) in the decommissioning the FM/FF cyclotron at the Institute for Nuclear Study, University of Tokyo. In the course of this study, it was found that ^{63}Ni produced by the ^{63}Cu(n,p) reaction provides a unique measure to estimate the fast neutron fluence of the atomic bomb. Thus, we proposed to determine ^{63}Ni in copper samples exposed to the Hiroshima atomic bomb as a method to estimate the fast neutron fluence [4], and measured the ^{63}Ni by liquid scintillation method [5]. The results obtained are consistent with the values calculated by the new Dosimetry System 2002 (DS02) [6]. Also, we measured the excitation function for ^{63}Cu(n,p)^{63}Ni up to neutron energy of ~7 MeV using the 4.5 MV dynamitron accelerator at the Fast Neutron Laboratory, Tohoku University [7], because it is crucial to estimate the fast neutron fluence from the amount of ^{63}Ni production.

In irradiation, the spherical copper shell was applied as a target material in order to measure cross sections continuously. The cross sections obtained were compared with the estimates by JENDL-3.3 [4], ENDF/B-VI [5], FENDL/A-2.0 [6]. The chemical separation procedure for nickel previously developed in the decommissioning the cyclotron was improved. Since the half-life of ^{63}Ni is 100y, 65% of ^{63}Ni produced by the atomic bomb still exists in the samples for more than 60 years after exporosion.

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17-TS2-1 17994

NUCLEAR ARCHEOLOGY IN A BOTTLE: EVIDENCE OF PRE-TRINITY U.S. WEAPONS ACTIVITIES FROM A WASTE BURIAL SITE

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During World War II, the Hanford Site in Washington became the location for U.S. plutonium production. In 2004, a bottle containing a sample of plutonium was recovered from a Hanford waste trench. Here, state-of-the-art instrumental analyses, reactor model simulations, and investigative science techniques were used to provide insights as to the origin of this unknown sample, a process collectively termed as nuclear archeology. Isotopic age dating conducted on the sample in 2007 indicated the sample was separated from the spent fuel 61.6 + 4.5 years earlier. The isotope ^{22}Na, a detectable product of a secondary nuclear reaction, proved useful as a powerful tool for nuclear forensic analysis as (1) an easily detectable signifier of the presence of alpha emitting actinides, (2) an indicator of sample splitting, and (3) a measure of the time since sample splitting. Analytical results of minor actinide isotopes and reactor model simulations confirmed the material originated from the X-10 reactor in Oak Ridge, TN. Corroborated by historical documents, we concluded this sample was part of the first batch of Pu separated at TPlant, Hanford, the world's first industrial-scale reprocessing facility, on December 9, 1944. This sample represents the oldest known collection of reactor-produced ^{239}Pu in the world.

17-S2-2 16788

INSTRUMENTAL DEVELOPMENT FOR MEASUREMENT OF ELEMENTAL DISTRIBUTION ON SWIPE SAMPLES FOR SAFEGUARDS

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The International Atomic Energy Agency (IAEA) has been collecting swipe samples from nuclear facilities all over the world during its routine safeguards inspections. Collected swipe samples are tested for some radiation measurements at a clean laboratory for safeguards before detailed analysis is carried out. In order to estimate distribution of uranium and the other elements on the surface of swipe samples, we have developed an X-ray fluorescence scanner. The scanner is able to analyze the swipe samples which are 10 x 10 cm^2 sheets of cotton under the atmospheric condition. The scanner consists of the following components: a 50-mm^2 Si detector with thermoelectric cooling module, a 50-W Pd X-ray tube with forced-air-cooling module and a sample changer. Compared with the detector and the X-ray tube with water-coolers, the scanner is more compact than similar instruments. The space required for this scanner is 90 cm x 75 cm.

The swipe sample is packed in a Ziploc plastic bag not to be spilled on the scanner. The sample fixed on a plastic frame and is measured horizontally in 280 positions by stepping motors. The detection limit of uranium is around 30 ng for each division when X-ray tube voltage and current are 50 kV and 1 mA, respectively.

17-S2-3 21421

DEVELOPMENT OF A HIGH PURITY GERMANIUM DETECTOR CLOVER SYSTEM AT LOS ALAMOS NATIONAL LABORATORY

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Members of the Nuclear and Radiochemistry group at Los Alamos National Laboratory are developing a High Purity Germanium (HPGe) clover system for highly sensitive non-destructive assay of a wide variety of samples by gamma spectrometry. This detector system consists of a pair of detector enclosures, each with 4 HPGe detector elements arranged in a four-leaf clover, for a total of 8 detectors. The two detector enclosures are arranged such that the endcaps face each other, with the ability to be positioned anywhere from contact to 45 cm apart. This is accomplished by a specially constructed stand, fabricated from low background man-made high purity materials. The clover detectors are surrounded by a custom-built Compton suppression detector. The entire system is located in a room fabricated from pre-World War II battleship steel.

Developed for the assay of specific isotopes in the presence of of naturally occurring radioactivity, this clover system design strives to achieve significant improvements in several key design areas, while still maintaining the level of operational ease that is necessary in a production counting lab. This presentation will focus on describing the design goals and trade-offs made in the development of the detector system, as well as the logistic and operational hurdles encountered in installing and bringing the system into initial operation.

17-S2-4 21545

FURTHER DEVELOPMENT OF A PORTABLE LIQUID SCINTILLATION SYSTEM WITH ALPHA/BETA DISCRIMINATION

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At the INL, we have been developing an extremely portable liquid-scintillation detector system with alpha/beta discrimination. With modern digital-signal-processor electronics, this unit has much of the functionality of a lab-based system, but is lightweight and requires only a laptop to operate. To optimize the portable nature of this system, we have tested various sample preparation techniques including the necessity of centrifuging and sparging the sample. Results will be presented, including detection limits.

17-S2-5 17856

SEQUESTRATION AND ANALYSIS METHODS FOR LANTHANIDES AND ACTINIDES USING RESONANCE IONIZATION MASS SPECTROMETRY

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We report on a rapid, high-sensitivity isotopic analysis method for lanthanides and actinides with minimal sample preparation. Solid samples are dissolved in acids and felements are sequestered from solution using ion exchange resins or magnetic microbeads ligand-functionalized. The beads are analyzed by Resonance Ionization Mass Spectrometry (RIMS). While the resins and ligands have high elemental specificity, the separation is not complete enough for analysis by conventional techniques that cannot resolve isobaric interferences. RIMS has the sensitivity to analyze trace quantities and the elemental specificity to remove isobaric interferences. We report on initial studies using Eu as the target element. Several resins, ligands and supports were investigated, at various Eu(III) concentrations and acidities. Mass spectra were obtained using the CHARISMA instrument at Argonne National Laboratory, which has been described elsewhere [1]. The spectra were obtained by rastering either an ion beam or a pulsed laser over the beads to remove Eu atoms from the surface, followed resonance ionization. A twolaser RIMS scheme was used: a resonance laser tuned to excite Eu from the ground electronic state to an excited intermediate state, and a second laser tuned for efficient ionization from the intermediate state. Ions were detected by time-of-flight.

Two different types of separations were investigated: ligand-functionalized microbeads and ion exchange resins. Microbeads showed efficient extraction at low Eu concentration. Di(diphenylphosphoric)imide (NP_2) modified beads, using 2-thenoyltrifluoroacetone (TTA) as a co-ligand, gave a quantitative sequestration of Eu(III), with 0.25 wt% beads removing > 97% of Eu at concentrations below 1 μM. At higher concentration, removal was less efficient due to limited sorption capacity. The co-ligand enhances the sequestration yield at high Eu loading: the addition of 3 μM TTA increased the extraction efficiency for 2 μM Eu(III) from 56% to 97%. For ion exchange we chose TRU-SPEC SPS resin (Eichrome). The extraction of Eu(III) was very rapid (< 5 min), but not quantitative (~10%), however this is mitigated by the large sorption capacity of ion exchange resins compared to functionalized beads. RIMS mass spectra were obtained from both functionalized beads and ion exchange resins. Excellent results were obtained on the NP_2-modified beads by depositing a film of the ~5 μm beads on a substrate and rastering a pulsed laser over a 75x75 μm area to remove Eu atoms from the surface. The measured isotope ratios were stable and reproducible; the precision obtained in one hour of analysis time was 0.4% (one sigma), with a chi-squared value of 1.0 over 27 separate measurements of the $^{151}Eu/^{153}Eu$ ratio.

Similar results were obtained on ion exchange resins, but in this case the 50 μm beads were analyzed individually. The precision in the $^{151}Eu/^{153}Eu$ ratio obtained in one hour of analysis time on a single 50 μm TRU-SPEC SPS bead was 0.4% (one sigma). Aggregating results from several beads gave a precision of 0.2% with a chi-squared value of 1.10.

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17-S2-6 14828

MEASURING FLUORINE IN URANIUM OXYFLUORIDE PARTICLES USING SECONDARY ION MASS SPECTROMETRY FOR NUCLEAR FORENSICS

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Gaseous uranium hexafluoride (UF_6) is used for the enrichment of uranium and is known to be a very reactive and volatile gas. When a small amount of UF_6 is released in the environment, it forms uranium oxyfluoride particles and hydrogen fluoride from the reaction with atmospheric moisture. The uranium oxyfluoride particles settle on various surfaces within or outside the enrichment facility where they are collected by safeguards organizations such as the International Atomic Energy Agency (IAEA) through a technique called environmental sampling. Despite their small size, the IAEA uses the uranium isotopic composition of these particles to determine whether an enrichment facility is compliant with its declarations. What makes samples from enrichment facilities particularly interesting is that they also often contain uranium particles with a measurable amount of fluorine. As uranium oxyfluoride particles lose fluorine over time and from the exposure to certain environmental conditions, the analysis of the relative amount of fluorine can place boundaries on particle exposure history.

For this work, we prepared a set of UO_2F_2 particle samples from the hydrolysis of UF_6 and stored these samples in environmental chambers at different temperature, humidity and lighting conditions. The NanoSIMS secondary ion mass spectrometer, having a spatial resolution in the order of 200 nm, was used to measure the F^+/U^+ secondary ion ratio of individual particles immediately after sample preparation, and at different time intervals. Scanning electron microscopy was used to evaluate the morphology of the particle samples before and after SIMS analysis. These measurements have shown that for samples stored in high humidity conditions, the F^+/U^+ secondary ion ratios were an order of magnitude lower than for those stored in dry conditions. A detailed study of the variations in the relative amount of fluorine will therefore contribute to an even more reliable interpretation of the analytical results.

COMPARISON OF IUPAC K0 VALUES AND NEUTRON CROSS SECTIONS TO DETERMINE A SELF CONSISTENT SET OF DATA FOR NEUTRON ACTIVATION ANALYSIS

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As part of an IAEA Coordinated Research Project we have compared k0 factors primarily from the IUPAC recommendations with prompt and delayed σ_γ values measured with guided neutron beams at the Budapest Reactor and/or derived from literature σ_0 and P_γ values to determine a self consistent set of values. A new library of k_0, σ_γ, and σ_0 values has been created. The library includes all known activation products and their decay γ-rays. Numerous discrepancies in these values have been found and will be discussed. Recent measurements aimed at resolving some of the discrepancies will be discussed.

18-S9-2 13039

DEVELOPMENT OF NUCLEAR IMAGE METHODS OF ANALYSIS BASED ON GAMMA ACTIVATION

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Nuclear methods based on registration of images for investigation of elements distribution (via correspondent radionuclides) in different samples have a long history. Neutron activation autoradiography is a common method, whereas gamma-activation autoradiography was not in use at all. In our recent works it has been demonstrated that the samples activation by bremsstrahlung radiation of microtron significantly exceeds the possibilities of neutron activation autoradiography for detection of noble elements micro inclusions in geological samples. A digital version of autoradiography has been developed.

In the recent investigations the attention was paid to development of such approaches of digital gamma-activation autoradiography which rationally complement quite effective non nuclear methods of local analysis. Among the developed approaches are: analysis of large size samples (dozens cm2) and development of software for extensive treatment of the autoradiographic images. Irradiation of large size thin section with their analysis is a promising method for fast detection of “zones of interest” containing elements in question while screening of samples series. The further detailed analysis of the selected small zones may be done for example, by SEM.

For uniform irradiation of thin sections in the field of bremsstrahlung radiation having quite narrow distribution a special device has been constructed. The device makes simultaneous rotation and alternate/reciprocal motion of the platform with the fixed thin section. To estimate the uniformity of the integral dose field a computer modeling the activation dose acquisition has been done. The agreement with experiment has been received. Small residual dose non uniformity (resulting from model of movement) is corrected mathematically by means of the developed computer program. To increase selectivity of the analysis by means of activation autoradiography a software for analysis of decay dynamics has been developed. The program loads a set of images obtained while sample cooling, loads necessary information on each image from data base and than estimates apparent decay constant for each pixel of the loaded images. As a result two new images are generated: apparent decay constant and residuals. The method permits fast and effective qualitative local analysis by means of activation autoradiography.

The developed procedures have been successfully applied for analysis of Pt-Pd micro inclusions in polymetallic ores of Norilsk area (North Eastern Siberia, Russia) having complex composition (Co-Ni-Sb-As mineralization with high concentration of Zn, Pb, Cu, Ni, Mn, Ag, Bi, Cd compounds).

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METALLOMICS STUDY：A NUCLEAR APPROACH

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Metallomics, as an emerging cutting-edge discipline, is an integrated biometal science, which refers to study the distribution, location, chemical species, structure, dynamics, and relevant biological effects of metal elements on organisms. It is attracting more and more concerns in scientific community, because it is closely related to human health and social welfare. The prerequisite for metallomics research is to establish the analytical methods with the features of high sensitivity, good selectivity, specific identification, and accurate quantification, which are constituting a true challenge. Nuclear approach, based on nuclear properties, nuclear structures, nuclear effects, nuclear reactions, and nuclear radiations, which highly rely on nuclear spectroscopy and nuclear facilities, has been and is playing important roles in studies of metallomics and metalloproteomics for their unique advantages, e.g. high sensitivity, excellent accuracy and precision, low matrix effects and good space resolution. They could provide important information on metal atoms in organisms, even in molecular or cellular level. A modern tendency for application of nuclear approach in metallomics and metalloproteomics is to combine different nuclear methods with different properties or to combine nuclear with non-nuclear methods to constitute hyphenated techniques. Some practical examples of the nuclear techniques in the metallomics field will be selectively outlined with the emphasis on the recent progress made in our laboratory along with their merits and limitations.

18-S9-4 14604

MEASUREMENT OF GEOLOGICAL SAMPLES USING NEUTRON ACTIVATION ANALYSIS WITH GAMMA-GAMMA COINCIDENCE

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The multiple γ-ray detection method developed for nuclide quantification has achieved better resolution and sensitivity than the ordinary singles gamma-ray detection method. The INAA combined with this method is called NAAMG (Neutron Activation Analysis with Multiple Gamma ray detection) 1-4) and has been successfully applied to various fields. In the case of neutron activation analysis, measurements of γ rays from trace elements are strongly interfered by the γ-rays from isotopes produced from major elements, e.g., ^{24}Na, ^{56}Mn. Therefore chemical separation processes are sometimes required to eliminate the major elements for determination of the trace elements. Measurements of iridium in geological sample were carried out by this method. Samples were irradiated at the JRR-3. Iridium concentrations in several standard rock samples and geological samples were also measured by this method. Fifty to one hundred mg of each sample were sealed in quartz tube and irradiated together with iridium standard. After irradiation, the γ-γ coincidence of multiple γ–rays from the Ir-192 was measured with the Ge detectors array, GEMINI-II. Gamma rays from about 10 ppt of iridium in geological samples can be detected by this method. (see in Figure)

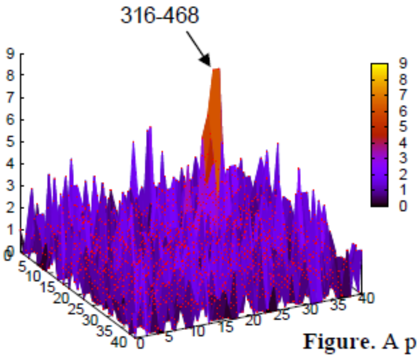

Figure. A part of 2 dimensional matrix obtained from 54.7 mg silicate rock sample. 316-468 keV coincident peak emitted from ^{192}Ir can be seen in the matrix. The silicate rock sample was irradiated for 48 hour at neutron flux of 9.8 x 10^{13} nsec^{-1}cm^{-2}. Concentration of iridium was determined to 18 ± 3 ppt.

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APPLICATION OF TRIPLE GAMMA COINCIDENCE IN PROMPT GAMMA-RAY ANALYSIS AND NEUTRON ACTIVATION ANALYSIS

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Prompt gamma-ray analysis (PGA) is a versatile element quantification method with non-destructive, rapid, high-precision and multi-element determination [1]. In actual application, however, the energy resolution of commercial Ge detectors is not sufficient and it is impossible to resolve all the gamma-rays, since the number of gamma-rays from the sample with multiple elements often exceeds one thousand. In a similar situation in Neutron Activation Analysis (NAA), we have applied a gamma-ray coincidence method (multiple gamma-ray detection method), and developed a new method of NAA coupled with Multiple Gamma-ray detection (NAAMG) [2-4]. Its high sensitivity is demonstrated in nuclide quantification [2-4]. The principle of the new method is described in Ref. [5].

We apply the multiple gamma-ray detection method to prompt gamma-ray analysis (Multiple Prompt Gamma-ray Analysis, MPGA) by using a new gamma-ray detector array [6] at a cold neutron beam line in Japan Research Reactor, JRR-3, at Japan Atomic Energy Agency (JAEA). In MPGA analysis we have used so far the gamma-ray double coincidence measurement as described in Ref. [5]. We firstly try to apply a triple coincidence measurement. The present detector system can afford the double and triple coincidence measurement as well as the singles measurement in PGA and NAA. In the presentation we will compare the detection limits for those measurements. Based on the results we discuss new applications to environmental samples.

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18-S9-6 16872

APPLICATION OF GAS PRESSURIZED EXTRACTION CHROMATOGRAPHY (GPEC) TO THE ANALYTICAL LABORATORY

Daniel Cummings, James Sommers, Marcos Jimenez and Jeffrey Giglio

The determination of analytes in radiochemical matrices is sometimes complicated by interferences. This is especially true in radiochemical, nuclear forensics, atomic spectroscopic and mass spectrometric measurements on irradiated samples. To facilitate the removal of interferences, a gas pressurized extraction chromatography (GPEC) system has been developed and applied to a wide variety of analytical challenges. The major benefits of the GPEC system are: that all liquid that is put into the system is recovered accurately and precisely; the columns have small internal volumes (35 to 85 µL) and are re-usable; the separations are more reproducible than drip column technology and are fast (typically less than five minutes per separation); the design incorporates a low pressure gas and liquid flow containment thus minimizing hazards and preventing contamination of radio-nuclides; it requires small volumes (0.25mL) of sample thus reducing personnel exposure and increasing flexibility of sample preparation options; and the GPEC system is amendable to automated separations (one automated version is routinely used).

This presentation will detail the methods development and results obtained from the application of the GPEC system to a wide variety of radiochemical matrices, sample types and instrumental detection schemes. These include the determination of major and minor components in post irradiation examination (PIE) fuel samples by inductively coupled plasma mass spectrometry (ICP-MS), the removal of U for determination of trace elements by ICP atomic emission spectroscopy, an improved actinide separation scheme for the determination of U and Pu by thermal ionization mass spectrometry and the removal of background species for radiochemical counting. In addition, the development of automated routine separations will be discussed.

19-PS1 21938

NUCLEAR AND RADIOCHEMISTRY EDUCATION IN THE U.S.A.: CRISIS OR TURNING POINT?

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During the past 20 years, a variety of professional societies have warned about the lack of highly-trained nuclear and radiochemists [1-6] to avert a potential crisis in meeting the nuclear–related challenges and solutions to our imminent lack of energy that may soon jeopardize the safety and wellbeing of our society. There is a great need for scientist with training in nuclear and radiochemical sciences, in frontier research and in a variety of applied areas including prediction and monitoring of behavior of radionuclides/actinides in the environment; nuclear medicine and isotope production; radio-pharmaceutical preparation; nuclear power, nuclear waste isolation and site remediation; treatment, processing, and minimization of nuclear wastes; ultra-sensitive instrumentation and analyses; automated and computer-controlled remote processing; stockpile steward ship, surveillance of clandestine nuclear activities and many other national and international security issues.

Several U.S Government organizations and selected Universities have recognized this tremendous need for fostering the education of nuclear and radiochemists by providing funding, although sometimes limited in scope, and creating new faculty positions.

This presentation will provide an overview of the current status on nuclear and radiochemistry in the U.S.A., discuss potential causes and solutions and analyze if the current measures are sufficient to alleviate this problem for the long-term.

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NUCLEAR FORENSICS: AN EMERGING AND STILL IMPERFECT SCIENCE

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Fingerprints and forensic analysis have played critical roles in criminal law for more than 100 years. In the relatively new field of "nuclear forensics" – which focuses on analyzing the nature, use and origin of nuclear materials – similar methods are applied to determine material characteristics with high degrees of accuracy. Just as with human fingerprinting, nuclear samples can be identified, examined and profiled. Measurements of radioisotopes, stable isotope abundances, “ages”, trace element impurities, chemical form and physical parameters can be assembled to create a "nuclear fingerprint". Nuclear forensic techniques applied to debris samples from a nuclear explosion can provide clues to the design of the device, the sophistication of the manufacturer and, perhaps, the method by which the device was delivered and emplaced. These same techniques applied to interdicted nuclear materials provide insight into the reactor and/or enrichment processes used to produce the sample, when the sample was last chemically purified, the intended use of the material and the country in which the nuclear material was manufactured.

Uranium ore concentrate (UOC), née yellowcake, is the final product in the mining and refining of uranium ore and represents an intermediate step in the utilization of uranium for energy and weapons production. Because UOC is a regulated nuclear material commercially traded worldwide, it provides an excellent test bed for nuclear forensic science. We are investigating chemical and isotopic signatures imparted on UOC by source rock and/or mining processes that have the potential to allow UOC to be traced back to its point of origin. This approach requires a library of sample analyses for comparison and the development of search engines to establish links between samples of unknown provenance and previously analyzed materials.

We have analyzed over 100 samples of UOC from locations worldwide for mineralogy, trace chemical impurities and U, O, Pb, Sr, and Nd isotopic compositions. Several significant trends are apparent. First, trace element abundances for UOC are often unique to specific locations and may be used, in conjunction with statistical analysis, to identify the origin of UOC. Second, U, Pb, Sr, and Nd isotopic compositions in UOC are only minimally affected by the milling and conversion processes and consequently can be tied to local geology. Third, the UOC samples exhibit small but systematic variations in $^{235}U/^{238}U$ ratios, providing a powerful new method to distinguish between low- and high temperature redox U-ore deposits. Efforts to integrate these observations to develop a predictive capability to identify sources of UOC are underway.

20-S2-2 21653

ACCELERATION AND AUTOMATION OF ACTINIDE ANALYSIS METHODS

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The isotopic analysis of actinides from complex matrixes such as environmental samples entails a multistep procedure. This procedure must bring the actinides into solution, separate them from the sample matrix, separate actinide elements from one another, and concentrate them for presentation as a source to a detector. Separations are required because, regardless of the detection method (radiometric or mass spectrometric), interferences of the isotopes with one another, and interferences of the matrix material with isotope detection, necessitate purification of the isotopes prior to detection.

Typically, samples are dissolved in acid solutions or by alkaline fusion. Subsequently, the matrix is separated by classical precipitation or solvent extraction methods. More recently, extraction chromatographic methods have gained widespread use. Separations of actinides from one another can be achieved through extraction chromatographic methods or by anion exchange, using sequences of eluents to release the actinides captured on the resin material. In some methods such as thermal ionization mass spectrometry (TIMS), actinides are purified on single beads, and/or transferred to single beads for source preparation.

Conventional manual methods for these procedures are tedious and time-consuming. Automation approaches offer considerable potential to accelerate these steps, reduce labor costs, and improve overall procedural consistency.[1]

However, given the diversity of methods used in completing a sequence of sample preparation and separation steps, no single automation approach meets all needs. Therefore, we have set out to create a set of automation approaches that can be used, as appropriate, and conducted in sequence for complete analytical processes. In this talk we will highlight specific approaches including the following methods.

For sample dissolution, with emphasis on total sample dissolution of sediments, we have developed a three stage microwave digestion approach.

For matrix separations, we are investigating extraction chromatographic methods. The automation of these column-based separation methods is a topic we have pursued for many years.[1] In our current studies, we are investigating separations with eventual TIMS detection in mind, and with the idea of processing several samples in parallel. These methods can isolate actinides from the matrix as a group, or selectively elute specific actinides.

We are also developing automation methods to perform column-based anion exchange separation methods. These classical separations remain useful for isolation of individual actinides; we have developed automated robotic methods to process samples in parallel.

Finally, to accelerate the microchemical purification of actinides on single beads, we have developed an acoustic streaming method that provides noncontact mixing in tiny volumes and can be done in parallel in microplates.[2]

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20-S2-3 17965

SURFACE ANALYSIS OF ELECTRODEPOSITED ACTINIDE SOURCES FOR ALPHA SPECTROSCOPY

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In order to perform high resolution alpha spectrometry, sources must be of high quality prepared by methods which give the most homogenous and thinnest deposition possible. Inhomogeneities and variable thickness will result in self-absorption and other such effects which cause energy loss within the sources. Electrodeposition has become the standard method of deposition due to its ability to produce thin layers, so thin however, that surficial characterization of inhomegenities and variable thickness can be very challenging to detect. Exploring the surface of several different alpha sources prepared under varying conditions will help determine the most efficient and appropriate plating technique. Proxy samples were created of depleted uranium using a Ti planchet backing and the plating method as described in Plionis et al. 2008[1], in quantities which would be applicable to the plating of higher actinides. The mass loading of electrodeposited planchets is typically determined by the activity of the isotope of interest. For these experiments the average mass loading for the higher actinides was determined to be approximately 145 ppb on a 3/16in diameter Ti planchet. This results in a concentration of 0.199μg/cm^2 of depleted uranium. Once the sample is plated, it is counted by alpha spectroscopy to determine the yield and actual mass of uranium. To determine what surficial features were produced in the electrodepostion process, an FEI field emission SEM with EDS and WDS capabilities was used. The SEM analysis showed dome like structures on the electroplated surface with an average diameter of 0.05μm. These dome features cannot be chemically identified by either EDS not WDS due to detection limits, but are believed to either be partially uranium based or to contain uranium within them. The ubiquitous layer of Pt seen by SEM indicates a potential threat to resolution and may result in thick enough layers as to cause energy loss resulting in low quality sources.

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20-S2-4 20259

DEVELOPMENT OF RAPID SEPARATION TECHNIQUES FOR NUCLEAR FORENSICS

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The rapid and reliable analysis of radioactive samples is extremely important in the case of a radiological or nuclear incident to provide much needed quantitative and qualitative information about the radionuclides released. A fast quantification of the amount of radioactivity released is required to estimate the exposure risk to the public and to allow for swift and informed decision making in the immediate aftermath of the incident. The rapid identification of the radionuclides released is necessary to permit attribution of the released radionuclides to a potential source. Information about the source of the radioactive material involved in the incident needs to be made available to intelligence agencies as quickly as possible. It is therefore necessary to develop sample analysis procedures that allow for a quick turnaround time and increased sample throughput with a minimum of deviation between samples. The analysis of samples for nuclear forensics requires the characterization of the total matrix by complete dissolution and subsequent chemical separations in addition to non-destructive analysis. This means the radioanalytical procedure applied does not only have to be rapid and reliable, it also needs to be able to handle the unconventional sample matrices that can be expected in the aftermath of a nuclear incident. It is therefore especially important to study the influence of matrix interferences on method performance.

The focus of our research is to evaluate 'off-the-shelf' vacuum assisted extraction chromatography technology for fast actinide separations in the presence of anthropomorphic/environmental matrices and in particular its potential for automation. Data from these experiments will provide both the physical (flow rate and lifetime) and chemical (kinetics and loading limits) boundary conditions necessary to proceed to the design and development of an extraction protocol suitable for automation. In this work, the extraction method was tested under varied flow rates and in the presence of common matrix interferences. Results thus far indicate that a rapid technique to separate the actinides from these interferences should be suitable for automation. To date, the reliable and efficient separation of Am/U/Pu, using stacked DGA, TEVA and TRU resins, has been demonstrated at varying flow rates ranging from 0.5-8 mL/min per mL of resin. Additionally, Am can be isolated from the interferences at a molar ratio of 1:10^6 (Am:interference). The rapid techniques described here have also successfully been used for the analysis of hot particles from the site of a nuclear weapons accident. The results show that the separation of interfering nuclides is not only invaluable for alpha spectroscopic measurements; it can also significantly reduce the limitations of gamma spectrometric analysis.

20-S2-5 21592

VALIDATION OF ELECTROCHEMICALLY MODULATED SEPARATIONS ON-LINE WITH MC-ICP-MS AS A MEANS OF RAPID LOW-LEVEL U-PU ISOTOPIC ANALYSIS

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Thermal ionization mass spectrometry remains the gold standard for the analysis of trace nuclear material for proliferation detection and verification of declared facility operations. The need for extensive radiochemical separations limits throughput and greatly increases the cost and complexity of analysis. The analysis of low levels of plutonium and uranium is possible by inductively coupled plasma mass spectrometry, but to date sample utilization efficiencies have been much lower than TIMS and the need for actinide separation and concentration prior to analysis is still necessary. For example, uranium hydrides and americium can interfere with Pu isotopic analysis, preventing resolution without separations. To increase throughput, chromatographic separations can be performed on line, but the requirement to change mobile phases and concentrations is not ideal for ICP-MS.

Electrochemically-modulated separation (EMS) of plutonium has proven to be quite robust and selective as an on-line separations technique for ICP-MS analysis of U and Pu. Utilizing a flowthrough electrochemical cell for preconcentration and matrix elimination, this approach offers a potential “electronic” alternative to ion exchange chromatography for selectively and rapidly isolating U and Pu from a sample matrix prior to isotopic analysis. Because the adsorption and release of U and Pu at an anodized glassy carbon electrode is controlled by the applied potential, the entire process can be completed in a simple matrix (2% HNO3) without the addition of any other chemicals. Volumetric preconcentration allows very small (<100 ag or <252,000 atoms of Pu) samples to be isotopically characterized on MC-ICP-MS without arduous preconcentration steps off-line. The results of a performance comparison between MC-ICP-MS and TIMS will be reported. Both EMS and ion-exchange chromatography will be employed for sample-clean-up.

Lastly, alternative EMS applications and an assessment of the “performance gaps” between MCICP-MS and TIMS will be addressed in regard to nuclear forensic analyses.

20-S2-6 16052

OPTIMIZATION OF Nd(III) PRE-CONCENTRATION ON A ROTATING DISK MERCURY FILM ELECTRODE IN AQUEOUS SOLUTION

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Typical analysis of environmental samples for nuclear forensic purposes requires digestion of the sample, pre-concentration of the analytes/isotopes of interest, and their subsequent separation, followed by quantification using either mass spectrometry or radiometric means. We have demonstrated that separation of the 4f-element cations can be achieved rapidly using capillary electrophoresis.[1] Capillary electrophoresis works from very small volumes, e.g. microliters or less. Thus, a method is needed to reduce sample volume, and ideally pre-concentrate the analytes of interest at the same time. Electroanalytical chemistry is a technique that offers the opportunity to significantly reduce sample volumes down to the micro- or nanoliter range, speed sample processing, and increase sensitivity by preconcentrating the analytes of interest prior to separations.

Current work within this lab indicates that trivalent lanthanides will consistently electro-deposit onto a rotating disk mercury film electrode in bulk aqueous solution thus allowing the user to pre-concentrate trivalent lanthanides for further separation. However, the mechanism of electrodeposition onto the mercury film is largely unknown, making it difficult if not impossible to predict *a priori* the conditions under which pre-concentration is optimized. In the present study, we explore some of the electrochemical factors affecting this pre-concentration process to optimize the technique for use in a wide variety of aqueous media. Trivalent neodymium (Nd(III)) is used as a model for the trivalent f-element cations. The factors to be discussed include rotation rate for the electrode, different deposition electroanalytical techniques, time effects, concentration effects, and the role of water in Nd(III) deposition.

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20-S2-7 20063

APPLICATION OF GUIDE TO THE EXPRESSION OF UNCERTAINTY IN MEASUREMENT (GUM) TO U AND PU ISOTOPE RATIO MEASUREMENTS BY THERMAL IONIZATION MASS SPECTROMETRY (TIMS)

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Proper treatment of analytical uncertainty associated with U and Pu isotope ratio and concentration measurements made on forensic samples increases the probability that the provenance of a given sample can be evaluated. Unlike traditional propagation of error, GUM (Guide to the Expression of Uncertainty in Measurement)-compliant data incorporates both random and systematic sources of uncertainty [1]. In this case, uncertainty refers to the dispersion of values that could be reasonably attributed to a measurand [2]. A rigorous estimate of the uncertainty that is inherent in all measurements increases the confidence in which these measurements can be used to determine sample provenance, a process critical in nuclear forensics.

We describe the process of creating GUM-compliant data using a set of U and Pu isotop measurements collected with an IsotopX Isoprobe-T thermal ionization mass spectrometer (TIMS). GUM analysis was used to produce uncertainty estimates for measurements of U and Pu isotopic ratios measured by total evaporation of untraced samples as well as uncertainty estimates for measurements of U and Pu concentrations measured via isotope dilution in multi-dynamic mode using Faraday and Daly detectors. We apply the principals of GUM to identify the measurand, identify and quantify sources of uncertainty, combine the significant uncertainty components, and produce an uncertainty budget using the software package GUM Workbench®.

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20-S2-8 22450

IMAGING AND MICROSCOPY TECHNIQUES IN THE EXAMINATION OF A PLUTONIUM HOT PARTICLE: APPLICATION TO NUCLEAR FORENSICS

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Evaluation of actinides in the environment provides opportunities to explore the use of novel methods for analysis with applications to nuclear forensics. Recent studies on plutonium hot particles collected after over 4 decades in the environment demonstrate the utility of microscopy in providing unique and valuable data to determine the source of the material. Results from optical microscopy, scanning electron microscopy (SEM), electron backscatter diffraction (BSC), energy dispersive X-ray spectroscopy (EDS), computed tomography (CT) imaging, and by experiments conducted at the Advanced Photon Source at ANL, including elemental mapping and X-ray absorption fine structure spectroscopy (XAFS) are presented. The data reveal enhanced information gained through the application of these techniques. Attention is given to the exploration of actinide speciation, behavior of stable elements, and identification of phases in the examined material. The utility of these techniques to better information nuclear forensics, especially when coupled with dissolutions method and traditional radiochemistry, is provided.

20-S2-9 19524

ANAYSIS OF SPENT RESEARCH REACTOR FUEL TO SUPPORT NUCLEAR FORENSIC PROGRAMS[1]

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Savannah River National Laboratory (SRNL) has been funded to analyze spent research reactor fuel assemblies stored at the Savannah River Site (SRS) to provide the data needed to determine the strengths and weaknesses of our reactor analysis codes to support the nuclear forensics mission. It is recognized that research reactor fuel is one of the least characterized sources of special nuclear material (SNM). Historical data on foreign and domestic reactor fuels are an important component of SNM attribution capabilities. Benchmark data is available for light water reactors (BWR and PWR), gas-cooled, graphite reactors, CANDU reactors, and LWBR fuel, as well as data from US production reactors (i.e. SRS and Hanford). There is little published data however on any of the many different Research and Test/Demonstration reactors that have operated worldwide. Instrumental measurement of SNM in research reactor fuel would broaden the knowledge data base on the least secure, least characterized class of reactor fuels. Intercepted SNM would likely not be from a known, well characterized source. For those cases, computational tools would be used to establish likely sources of the material. Reactor modeling of measured research reactor fuels would demonstrate the utility of the computational tools to identify the likely source of any intercepted SNM and would enable attribution laboratories to establish the strengths and deficiencies their reactor analysis codes.

To perform nuclear forensic quality analyses on spent research reactor fuel requires careful consideration of many aspects. The associated dose rate required that the assembly chosen for analysis be handled remotely and initial sample collection performed in Shielded Cells. The SRNL Cells have been used for over 50 years to provide research support to the production and now waste disposition activities associated with the SRS thus the Cells have significant legacy contamination. An Isolation Box was designed so that the assembly could be remotely handled in a clean environment inside the contaminated Shielded Cells. Sampling techniques were developed to collect a subsample of the assembly; the subsample was then dissolved and diluted in the Isolation Box to provide aliquots to the analytical labs for analysis. To perform some high precision analyses, such as the U and Pu isotopic measurements and rare earth isotope ratio determinations, initial sample purification was performed in radiologically controlled laboratories and then measurements made using clean instruments. A description of the sample collection and subsequent analyses will be presented.

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ISOTOPE RATIO TECHNIQUES TO DETERMINE ENERGY PRODUCTION IN REACTORS

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The measurement of characteristic radiation from fission products or activation products has long been used to infer neutron fluence in reactors. We have developed direct-analysis methods to achieve this goal by utilizing secondary ionization mass spectrometric (SIMS) analyses of irradiated reactor materials. All reactor materials contain trace elemental impurities at various levels, and the isotopes of these elements are transmuted by neutron irradiation in a predictable manner. Assuming initial values for isotope ratios, the changes in isotope ratios may be measured to determine fluence and energy production; initial element or isotope concentrations are not needed. This approach has been successfully demonstrated on graphitemoderated reactors and on samples taken from metal structural components from reactor cores, and has useful nuclear forensic applications and applications in nuclear safeguards monitoring. Indicator impurity elements should exist in sufficient quantities to be accurately measured, have stable activation products, and have cross-sections of suitable magnitude to result in meaningful isotope ratio changes for the fluence range in question. For high-fluence reactors, Ti^{48}/Ti^{49} and $^{179}Hf/^{176}Hf$ ratios are useful, and B^{10}/B^{11} ratios are excellent for low-fluence ranges.

Graphite reactors are particularly well-suited to such analyses since the graphite moderator is resident in the fuel region of the core for the entire period of operation. We have studies samples of graphite from two reactors with cumulative burnup of 0.8 to >30 GWd/MT, and samples of aluminum alloys and zirconium alloys from other reactors. In the latter sample study, samples of irradiated zircaloy were cut from channels surrounding a Boiling Water Reactor (BWR) fuel assembly. The declared range of the assembly average exposure was approximately 35 to 44GWd/MT.

In a light water reactor, the interpretation of results may be dependent on coolant density, which depends on the location of the sample in core. The use of two or more isotope ratios allows the water density at the sample location to be inferred even when using an approximate two-dimensional reactor model.

TRACE ELEMENTAL ANALYSIS CAPABILITIES FOR THE CHARACTERIZATION OF RADIOACTIVE AND STABLE ISOTOPES FROM AEROSOL PARTICLES ON MARPLE SUBSTRATES

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Personal air sampling cascade impactors are useful for collecting aerosolized particles in a variety of situations. These devices utilize a battery-operated pump to drive air across nine successive stages in an effort to separate aerosolized particles into size fractions by their activity median aerodynamic diameter (AMAD). During sampling, incident particles are impacted onto one of nine separate marple substrate stages. These marple substrates provide a convenient means by which multiple analytical routines can be simultaneously conducted in order to determine the airborne concentrations of a vast suite of radioactive and stable isotopes.

Prior to the sampling activity, accurate initial masses for each substrate are determined using a microbalance. After the sampling is concluded the substrates are again weighted to determine a gross gravimetric yield. Each substrate is then counted with either a high purity germanium (HPGe) detector or an alpha spectrometer to identify and quantify the presence of gamma-ray or alpha-emitting isotopes. Following these non-destructive techniques, each substrate is then cut into six equal fractions for a series of destructive analytical measurements.

During the destructive analysis process, a fraction of each marple substrate is added to a liquid scintillation cocktail capable of dissolving filters and counted for gross alpha and beta activity. Another fixed fraction of the sample is analyzed by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) or micro x-ray fluorescence in order to characterize the morphology and map the elemental composition of the impacted particles. In combination, these analytical capabilities permit the determination of virtually all elements with $Z \leq 13$. About half of the sample substrate of each marple is either digested or leached with strong acids and analyzed by inductively coupled plasma atomic emission spectroscopy and mass spectrometry (ICPAES/ICPMS) and thermal ionization mass spectrometry (TIMS). A portion of the sample is always archived for further analysis, if necessary. Analytical techniques, challenges, and results of uranium and plutonium particles collected on marple filters will be discussed.

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THE FORENSIC ANALYSES OF URANIUM OXIDE PARTICLES FROM THE COLONIE ENVIRONMENTAL CASE-STUDY

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Between 1958 and 1984, uranium metals were processed at a National Lead Industries (NLI) plant in Colonie, NY, USA. Combustion of scrap metals resulted in emissions of uranium particulates into the environment. Soils and dusts surrounding the NLI site were contaminated by the aerial deposition of c. 5 tonnes of depleted uranium from episodic stack emissions that were initially dispersed by prevailing winds. [1]

Individual particles have been isolated from soil and dust samples. These have been imaged and characterised by scanning electron microscopy (SEM), and by extended X-ray absorption fine structure (μEXAFS) spectroscopy. Hollow spheres of polycrystalline uranium oxides, with diameters 30 – 60 μm, are a distinctive particle morphology from these samples. They are similar to particles produced by depleted uranium munitions impacting armoured targets, and can be attributed to the autothermic oxidation of melt droplets. The compositions of the analysed spheres are mainly UO2+x and U_3O_8. These particles have survived more than 25 years in the terrestrial environment, as some of the least bioaccessible phases of uranium. [2]

Laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) has been used to analyse $^{235}U/^{238}U$ and $^{236}U/^{238}U$ ratios from 115 individual grains [3]. Relative uncertainties (2σ) of c. 0.4 and 2.7 % respectively are sufficient to resolve trends between isotopic compositions. The analytical methodology is rapid and requires minimal sample preparation; it is therefore attractive for nuclear forensic applications.

All of the uranium oxide grains were from depleted uranium. The $^{235}U/^{238}U$ ratios spread from (1.5 - 2.4) $x10^{-3}$, and for $^{236}U/^{238}U$ from (5 – 31) $x10^{-6}$. These variations were attributed to differences in feedstocks handled at the NLI site. The isotopic signatures have been compared with the tails assays from the Paducah Gaseous Diffusion Plant (PGDP), with which they are highly compatible. To verify the origin of the Colonie DU, $^{234}U/^{238}U$ was measured from a sub-set of the particles. It is now possible to identify six batches of PGDP by-product, from specific months, which account for most of the isotopic variations from the Colonie particles. [4]

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20-S2-13 22061

RECENT DEVELOPMENT WORK ON NUCLEAR FORENSIC SIGNATURES IN NATURAL URANIUM

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Natural uranium is the starting material for the production of nuclear fuels. Uranium of natural isotopic composition is mined from uranium containing ores in different geological formations. The uranium is extracted, chemically purified and pre-concentrated. As an industrial scale material, uranium ore concentrates will carry signatures that provide information on the history and on the origin of the uranium. These signatures may be source material inherited or process inherited. In the present work we investigated the significance and potential application of parameters such as the rare earth elemental patterns or strontium and lead stable isotope ratios. The methodology developed and its application to uranium ore concentrates from different mines around the world will be presented.

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NUCLEAR FORENSIC SIGNATURES IN COMMERCIAL NUCLEAR FUELS

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Partnerships with commercial fuel fabricators provide a unique opportunity to tie specific signatures to manufacturing processes by learning their specific processes, analyzing the fuel pellets resulting from those processes, and reviewing historical quality control data for variation in materials characteristics over time. Understanding these signatures allows us to further our understanding of the signatures that might be present in other fuels (foreign, HEU) whose production methods are less accessible. We have recently analyzed samples of fuel pellets from 3 commercial fuel fabricators for isotopic composition, trace impurity content, and surface and microanalytical characteristics. We then compared our results with those expected from our knowledge of each fabricator's production process.

Using ICP/MS to determine each pellet's age has already proved to be a powerful signature, with the ability to date individual pellets to within 1-2 months (depending on the amount of U3O8 add-back). In a recent analysis of a paired powder and pellet samples, though, we determined an age of ~8 years, which seemed to be too old. After discussing our findings with the manufacturer, we learned that the lot of material included ~30% of blended-down HEU. The age analysis allowed us to gather unexpected insight into the origin of the material.

Because fuel pellets are extremely clean, any impurity present at a level of tens of ppmw or higher is related to process. Trace impurity analysis of these fuel pellets has shown that materials used in the fabrication process, such as pore formers, mold release agents, and burnable poisons often show up as trace impurities in the pellets. Surface contaminants can convey information about further pellet processing, e.g., firing, grinding, and cleaning.

Oxygen isotopic analysis provides a potentially powerful geolocation signature. However, it is first necessary to understand the combined effects of process water (whose oxygen isotopic composition varies in a known way with geography) and of subsequent fractionation during conversion and fuel fabrication. In fact, differences between the oxygen isotopic composition of the fuel pellet and process water can provide information about the conversion process itself, specifically the temperature of the process.

Finally, analysis of the historical data from one fabricator has shown the challenges in utilizing third-party databases for nuclear forensics. The database has many artifacts from the analytical measurement process, including baseline shifts and abrupt changes in variability. Furthermore, we expect many signatures from impurities present at less than the fabricator's detection limit.

PRECONCENTRATION OF COPPER BY CLOUD POINT EXTRACTION WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL AND DETERMINATION BY NEUTRON ACTIVATION

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A method for the preconcentration of Cu(II) by cloud point extraction (CPE) followed by its determination using neutron activation analysis (NAA) has been developed. The method involves the use of a nonionic surfactant, namely polyoxyethylene nonylphenyl ether (PONPE-20), and a chelating agent 1-(2 pyridylazo)-2-naphthol (PAN). A phase diagram of the surfactant has been constructed and the effects of different additives on the cloud point have been investigated. Factors, such as the solution pH, ionic strength, temperature, and concentrations of chelating agent and surfactant which can influence the extraction efficiency of the metal have been optimized. The Cu(II) chelate has been extracted into a surfactant-rich phase of small volume with a recovery of nearly 100% and a preconcentration factor of 60. The method has been applied to tap water samples. The irradiations were performed at the Dalhousie University SLOWPOKE-2 Reactor (DUSR) with a nominal neutron flux of 5×10^{11} cm^{-2} s^{-1} in the inner pneumatic sites. The sensitivity for Cu by NAA was found to be 720 counts μg^{-1} using a t_i=10 min, t_d=1 min, and t_c=10 min. The detection limit for Cu has been found to be 1.5 ng.g^{-1}. The details of the development of the method, precision and accuracy of measurements, and results will be presented.

NEW FEATURES OF HYPERGAM FOR HPGE γ-RAY SPECTRUM ANALYSIS

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The HyperGam program has been developed for automatic analysis of complex HPGe γ-ray spectrum. The main functions are peak search, peak area determination and fitting. The semiautomatic analysis algorithm for γ-ray peak is adopted from a well-known peak analysis code, HYPERMET [1]. Basic features such as automatic peak search, nonlinear fitting of multiplet peaks have retained. Window based graphic user interface is provided on MATLAB platform and nuclide identification, MCA emulation and peak monitoring are incorporated for the full-automatic analysis. An example of HyperGam in ambient gamma radiation monitoring is shown [2].

For boron analysis in Prompt Gamma Activation Analysis, a Doppler-broadened peak (DBP) analysis routine has been added [3]. Since the shape of DBP depends on a phenomenological stopping power of the sample medium, several numerical routines for convoluting HPGe detector response are developed and algorithms for least-square fitting to the measured DBP are incorporated. An example implementation of the routine analysis of ^{10}B is presented on the HyperGam.

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UNCERTAINTY OF GAMMA-RAY PEAK INTEGRATION

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Because of their superior resolution and thereby superior qualitative and quantitative analytical capabilities, HPGe detectors have supplanted scintillation detectors wherever the necessary refrigeration apparatus is acceptable. The essential step in interpreting gamma-ray spectrometry data is the detection, identification, and quantitative integration of significant peaks in the spectrum. It is an open question1 whether most spectrum analysis software could survive a formal quality audit with regard to reproducibility and documentation. Intercomparisons involving standard spectra generally have shown that operator experience, related to calibration and the choice of significance parameters, can be as important as the particular algorithm used. The present work is an attempt to evaluate precision and bias of several software approaches under routine conditions.

Manganese-56 was selected as a demonstration case. The abundances of its seven significant gamma rays decrease monotonically with increasing energy, such that the area of the principal 847 keV is 1600-fold larger than the peak at 3370 keV. Furthermore, its convenient half-life of 2.5789 h permits numerous repeated counts during a reasonable decay time to examine counting-rate effects and detection limits. Ge spectra were acquired every 30 minutes for 19 h, during which time the source decayed by a factor of 170. The resulting spectra were interpreted by three commercial peak-search programs operating under VMS and Windows operating systems, and by SUM,[2] a fixed-boundary integration program long in use at NIST. These programs were compared with regard to their ability to follow the source quantitatively as it decayed. The results will be discussed with regard to the reliability of uncertainty statements.

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NON-DESTRUCTIVE ANALYSIS OF BULKY METEORITES BY NEUTRON-INDUCED PROMPT GAMMA–RAY ANALYSIS

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Introduction Neutron-induced prompt gamma-ray analysis (PGA) is a non-destructive analytical method applicable to solid materials. When PGA is performed by using neutrons guided out of the nuclear reactor, the neutron flux can be considerably low and, hence, the residual radioactivity level after proper cooling is so low that the sample once used for PGA can be safely reused for other research purposes. Considering the preciousness of meteorite samples, PGA can be the most suitable analytical technique for bulky meteorites. In analyzing solid, bulky samples by PGA, neutron absorption and scattering as well as gamma ray attenuation in the sample can occur and need to be corrected if such effects cannot be ignored [1]. In this study, as a part of setting an analytical protocol or the accurate determination of chemical composition of bulky meteorites by PGA, the effects of neutron absorption and scattering are studied.

Experimental For evaluating the effect of neutron absorption, the following experiment was conducted. Four geochemical reference samples (JA-1, JB-2, JG-1 and JP-1) were sealed in FEP film bag. The sample mass was increased from 200 mg to 1 g for each sample to monitor the change of elemental sensitivities due to the variation of bulk absorption and scattering cross sections of the samples (varying from 0.62 to 1.41 b and 4.42×10^{-3} to 7.6×10^{-3} b, respectively). The neutron scattering caused by H was also evaluated by analyzing JB-2 mixed with oxalic acid. Each sample was irradiated by guided beam of thermal neutrons for about two hours at JRR-3M of JAEA.

Results and discussion We found the sensitivity change depending on the content of elements. The sensitivities of H, Al, Ca and Fe were observed to decrease with increasing of thickness of diskshaped JB-2 with 3.57% H concentration, whereas the sensitivities of Si, Sm and Gd remain constant within the errors associated with counting statistics. Sensitivity enhancement due to the increase of H concentration in oxalic-acid-doped JB-2 was observed for the elements such as Fe, Mn, Si, Al, Ca, K, Sm and Gd.

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COMPARATIVE STUDY FOR AIRBORNE TOXIC METAL DETERMINATION BY INAA AND CCT-ICP-MS

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Although toxic elements are minor components in the atmospheric environment, they play a significant role as important marker for atmospheric science such as risk assessment, long-range transfer study, and source apportionment. Therefore, the techniques, which allow accurate and fast elemental analysis with a minimum pre-treatment, are very important. INAA has a main advantage of non-destruction of air particulate samples, while inductively coupled plasma with mass spectrometry (ICP-MS) encounters the most significant difficulties in pre-treatment (digestion, fusion, and dilution) and polyatomic spectral interferences for interest toxic elements. Although INAA is still reference method, a number of factors (disadvantages of cost, complexity of the instruments, and scarcity of nuclear reactor) limit its applications. To date, the use of collision cell technology ICP-MS (CCT-ICP-MS) is recommended instead of typical ICP-MS for the analysis of the toxic elements; this is because CCT-ICP-MS technique prevents polyatomic spectral interferences despite of contamination and volatile effects. [1] A series of experiments was conducted to test the compatibilities of two different techniques to determine concentrations of eight toxic metals (As, Cd, Cr, Mn, Sb, Se, V, and Zn) by INAA and CCT-ICP-MS based on both the NIST SRM 2783 (air particulate on filter media) and the field samples for PM10. For NIST SRM, the results of INAA were more accurate and precise for all target elements than those of ICPMS.

The comparative data set for PM10 samples collected in an industrial complex area showed that mean of concentration ratio, derived for the two different methods such as C(INAA/ICP-MS), were exhibited between 0.8 and 1.2 for all target metals. For in-depth study, analytical results obtained from both methods were evaluated in terms of regression analysis, paired t-test, and Wilcoxon signed-rank test. Standard uncertainty factors were also examined for the both analytical techniques. Analytical expanded uncertainties for INAA and CCT-ICP-MS were evaluated and discussed.

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LARGE SAMPLE NAA BY K0-BASED INTERNAL MONO STANDARD METHOD USING IN-SITU DETECTION EFFICIENCY

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Large size (in g-kg scale) sample analysis plays an important role for better analytical representativeness compared to routinely analysed small size (10-500 mg) samples. Due to high penetration power of neutrons and γ-rays, Neutron Activation Analysis (NAA) using low flux reactor neutrons is a suitable technique for large sample analysis. In practice, the problem associated with large sample analysis is neutron flux perturbation and gamma ray self attenuations. The k_0-based internal monostandard NAA (IM-NAA) in conjunction with in-situ detection efficiency, standardized in our lab, overcomes the above two problems provided the sample is homogeneous. In our ealier studies, we have analysed large size samples of metals and alloys like 1S-Al, zircaloys and stainless steels as well as food grains [1-3].

The paper deals with characterization of thermal column irradiation positions at Apsara/Cirus reactors at BARC, Mumbai and validation of IM-NAA method using synthetic samples and reference materials. Large size (10-250 g) samples of soil and ores (including uranium ore) as well as small size samples (50 1000 mg) were analysed to arrive at representative sample size and to understand heterogeneity associated with small size samples. Large and small size samples were irradiated using thermal column and core positions of Apsara reactor respectively and assayed using high resolution γ-ray spectrometry. In-situ detection efficiency in the range of 122-2112 keV was carried out using γ-rays of the activation products namely ^{152m}Eu, ^{140}La, ^{72}Ga and ^{56}Mn. The elemental concentration ratios with respect to Na (internal standard) reveal that samples of about 1 g and above are the representative samples for analysis. This work was carried out under IAEA Coordinated Research Project CRP (Code : F2.30.27).

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21-TS3-7 20142

IMPROVED COMMITTED EFFECTIVE DOSE ESTIMATES FOR URANIUM FOUNDRY PROCESSES USING MARPLE CASCADE IMPACTORS

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Inhalation and deposition of uranium particles into the lungs poses a significant chemical and radiological health hazard to uranium foundry workers. Due to the fact that the natural isotopes of uranium have a very long physical half-life and, depending on chemical form, a long biological half-life, the committed effective dose (CED) to a worker after an accidental inhalation may be significant. In addition, the size of the inhaled particles is known to have a variable effect on the CED due to varying size-dependent deposition and incorporation patterns. While many inhalation dose models assume a single generalized particle size to determine CED, foundry processes are known to produce a variety of particle size distributions. Sophisticated inhalation dose models are able to utilize previously determined particle size distributions to better model the CED that would result from an accidental inhalation intake involving a specific foundry process.

Personal air sampling cascade impactors are useful for collecting aerosolized particles during foundry operations. These devices utilize a battery-operated pump to drive air across nine successive stages in an effort to separate aerosolized particles into size fractions by their activity median aerodynamic diameter (AMAD). During sampling, incident particles are impacted onto one of nine separate marple substrate stages. These marple substrates provide a convenient means to determine airborne uranium air concentrations and particle size distributions. Individual marple substrates can be counted by alpha spectrometry in order to identify and quantify uranium isotopes.

In this work, three foundry processes were studied: hot forming, rolling, and lathing. Median particle size was shown to vary from 0.8 to 12.0 μm. In addition, lognormal, bimodal, and trimodal distribution patterns were observed for the different processes. The implications of applying this data to CED estimates will be presented.

USING SOILS FOR ACCIDENT DOSIMETRY: A PRELIMINARY STUDY USING OPTICALLY STIMULATED LUMINESCENCE FROM QUARTZ

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It is well known that natural minerals exposed to ionizing radiation emit luminescence, i.e. thermoluminescence (TL) or optically stimulated luminescence (OSL), on subsequent exposure to heat or light, respectively. These luminescence signals are widely used for dating and retrospective dosimetry. Presently, a single-aliquot regenerative-dose (SAR) OSL protocol is considered to be the robustest protocol for determining dose absorbed by quartz. However, Tsukamoto et al. [1] showed that there were several problems in applying SAR method to unheated volcanic quartz. In this study, a SAR protocol was developed specifically for measuring background dose in natural quartz extracted from soils collected around Tokai-mura in Japan. The objective was to assess the potential of using soils for retrospective assessment of a radiation accident. Moreover, variation in dose with depth was also measured. In an active soil, the background dose in a soil sample is a complex function of grain mobility and the mean bleaching depth (for a constant dose rate). In a relatively non-active soil, however, the shape of the dose-depth profile is a function of the bleaching depth. Therefore, decoupling an accident dose-depth profile from a soil section could be non-trivial. For this reason, we also investigated on the variation of background dose with soil depth in our soil sections.

The SAR data showed good reproducibility and dose recovery, and there were no evidence of fading of quartz signal based on the 'delayed' dose recovery experiments. The dose of minimum detection limit (MDL) was 0.1 Gy.

The dose dependence was measured both using the above SAR OSL protocol, as well as a SAR TL (violet emission) protocol. The background doses were generally the range of the MDL – few Gy, and no clear trend in dose depth profile was observed. An absence of clear trend might be indicative of ongoing soil activity resulting remixing of grains from the surface. Detailed results and conclusions of these investigations will be presented at the symposium.

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ORIGINS OF SEASONAL OSCILLATIONS IN RADIOACTIVE EXPONENTIAL DECAY

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Several investigations provided evidence for the seasonal (winter-summer) oscillations superimposed on the radioactive exponential decay curves. The relative amplitudes of the oscillations were between approximately 10^{-3} and 10^{-2}. They were seen in the decay of ^{226}Ra and daughters measured in an ionization chamber, ^{32}Si + ^{32}P and ^{36}Cl measured in the gas proportional detector, ^{152}Eu measured on a Ge(Li) detector, ^{56}Mn measured on a NaI detector, as well as ^{119m}Sn and ^{125m}Te Mössbauer sources measured using a NaI detector. Attempts were made to explain some of these oscillations with basic, often exotic physics.

In this work, we derived simplified models of gas detectors to elucidate several of these effects. In the case of the ionization chamber, we have shown that the oscillations can be explained by the change of argon density inside the chamber caused by the temperature change. Higher average summer temperatures in the laboratory decreased argon density at constant pressure, thereby lowering γ-ray absorption, which resulted in lowering of the counting rate in the summer as compared with the winter.

We also derived a model of a gas proportional detector, consisting of an air absorber, window, and the detector volume. We have shown that the oscillations can be explained by the effect of the temperature on the absorber air density between the radioactive source and the detector, when the detection system operated in such a way as to maintain the air pressure constant. Higher summer temperatures in the laboratory decreased the air density, causing less absorption of β particles in the air and resulted in higher counting rates in the summer as compared with the winter.

We have also shown that other effects such as humidity, background, muon flux, and radon concentration did not have any great effect on the seasonal oscillations of the counting rates. The models described in this work were approximate and they utilized principles of ionizing radiation interaction with the matter. Despite the necessity to make several assumptions, as well as incomplete information about the original experiments, our calculations provided semi-quantitative agreement with the oscillation amplitudes in the published data. More sophisticated detector models or Monte Carlo simulations are required for detailed study of the counting rate oscillations.

In addition to detailed modeling of the gas detectors, we suggested that the oscillations seen in the NaI detector measurements could be due to known relatively high sensitivity of NaI to the ambient temperature.

21-S3-10 19926

TRITIUM MEASUREMENT BY USING A PHOTO-STIMULABLE PHOSPHOR BaFBr(I):Eu^{2+} PLATE

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An imaging plate (IP) made of europium-doped BaFBr(I), a photostimulated luminescence (PSL) material, is a two-dimensional radiation sensor. Many excellent properties of the IP such as a wide dynamic range, a high sensitivity, and a high resolution have been making it possible to apply the IP to measure various types of radiations in different fields so far [1, as an example]. Recently, the IP has been successfully applied to determine the surface tritium distribution of in-vessel components of plasma devices [2]. Tritium measurement is indispensable for fuel processing systems of DT-fusion facilities. Tritium emits beta particles with a maximum energy of 18.6 keV and an average of 5.7 keV. The betas have a range of about several micrometers in matter and hence the technique is sensitive to tritium in the depth of a few microns. The tritium IP technique detecting the beta particles is unsuitable for use in deeper regions than the escape depth of beta-rays from tritium. Then, a new approach to detect tritium utilizing bremsstrahlung induced by tritium beta-rays is being developed. The measurement principle of this type of tritium detector is observing the bremsstrahlung X-rays generated by the interaction between beta particles from tritium and matter, on the basis of X-rays penetrating materials much more easily than weak beta rays of tritium with the maximum energy of 18.6 keV.

In the present study, the characteristics of the IP for the measurement of tritium detecting the bremsstrahlung X-rays from tritium were examined. The results were compared to those by detecting the beta particles. Measurements were conducted by using a small borosilicate glass tube, filled with pure tritium gas and a tritium beta-rays source as each radiation source. The fading effects of the IP were investigated for both types of radiations and functional equations that include two variables: elapsed time (t) and temperature (K) have been developed.

[1] H. Ohuchi, T. Satoh, Y.Eguchi, Y. Kaga, T. Arai, S. Suzuki, A.Yamadera, Skin dose measurement for patients using Imaging Plates in interventional radiology procedures, Health Phys. 93(1) (2007) 78-86.
[2] T. Tanabe, V. Philipps, Tritium detection in plasma facing component by imaging plate technique, Fusion Eng. Des. 54 (2001) 147-149.

GAMMA RAY DOSIMETRY IN A ^{60}CO IRRADIATION CHAMBER WITH A SMALL PIECE OF CWO SCINTILLATOR AND GAP PHOTODIODE

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Real time and remote measurability of a radiation dosimeter provides a great convenience in the circumstance that the radiation dose to be delivered to an object is large. When a high spatial resolution is required in the dose measurement, the sensor size should be as small as possible. It has been suggested that a fiber optic-based scintillation detector can meet these requirements all together.[1] In this work, a radiation dosimeter model is constructed by combining a small cylindrical piece of CWO(CdWO4) scintillator, a plastic optical fiber and a GaP photodiode. The lights generated in the scintillator are transferred through the fiber to the photodiode, which converts them into the electric current. The photodiode and optical fiber respectively provide real time and remote measurability, and high spatial resolution is offered by the small size of CWO.

The scintillator head is inserted into an irradiation chamber loaded with about 220TBq of ^{60}Co and the electric currents are measured at a number of points between the source and scintillator. MCNPX simulations are conducted for the same detector-source arrangements to calculate the absorbed energy in the scintillator. Assuming that the calculated values are reference ones, proportionality is investigated of the photodiode current with respect to the energy deposition rate. A commercially available Farmer-type ion chamber of volume 0.6cc is also employed to measure the air kerma dose rate at the same points. A normalized distribution of the photodiode current is compared with those of the energy deposition rate and ion chamber measured dose rate to investigate how accurately the dosimeter model measures the change of the absorbed dose rate as a function of the dosimeter-tosource distance. A best fit calibration factor or formula is derived, which can be used to convert the photodiode current into the dose rate, and error analysis is made of the calibration.

[1] LiF:W as a scintillator for dosimetry in diagnostic Radiology, R. Nowotny, 2004, Phys. Med. Biol. 49, 2599–2611.

21-S3-12 17245

APPLICATION FOR SIMPLE AND QUICK CALCULATION OF AVIATION ROUTE DOSES

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Pilots, flight attendants, and passengers aboard airplanes are subjected to higher cosmic radiation levels than that on the ground level because of high altitude. Extra doses due to flight is a so called "aviation route dose". Corresponding to the needs of estimating aviation route doses (Sv), the application developed in this project provides dose rate (Sv/h) distribution along the flight route and aviation route dose. Public user can use this application through the website. User friendly interfaces made with Adobe Flash provide functions to select airports on dynamic map or to search by airport/city names, and to report resulting aviation route doses and graphs of dose rate change through the flight.

This application consists of the dose rate calculation module and the airport database. First, the user selects airports for departure and arrival from the airport database that contain approximately 4,000 airports all over the world. Second, the user selects flight date. The application then, derives the great circle flight route. Dose rates along the flight route are then derived on every 10 minutes in total flight time by interpolation from dose rate matrix of cut off rigidity, Rc (MV) and Force Field Potential, FFP (GV). Aviation route does are derived from integrating dose rates by flight time.

Ordinarily, the process to derive dose rate consists of fluence calculation of particles including neutrons, protons, Helium nucleous, muons, electrons, positrons, and photons on each energy level, Rc, and FFP followed by multiplication with dose conversion factors [1] and summation. The PARMA model [2] released to public from Japan Atomic Energy Agency solves this process. In this project dose rate data on the ground level and three cruise altitudes at several Rcs and FFPs were calculated in advance using EXPACS and stored in the server as matrix data. Instead of following ordinary calculation process each time user requests, interpolation using dose rate matrix substantiates simple and quick calculation through internet.

FFP reflects tendency of solar activity. Selection of flight date extracts corresponding FFP from FFP database. FFPs are preliminarily derived using neutron monitor data provided from several places over the world [3] and stored into FFP database. Rc varies by positions on the earth. Rc values at every one degree latitude and longitude were preliminarily derived by MAGNETOCOSMICS [4] code released to public from Bern University and stored into Rc database. Each flight extracts Rcs along the route from Rc database.

It is not easy for public users to obtain actual latitude, longitude, altitude, and velocity of their flight, and sometimes the user would like to evaluate fictitious flights. Therefore this application applies abstraction of conditions such as empirical velocity and typical cruise altitudes of 28,000 ft, 36,000 ft, and 40,000 ft. It is assumed that change of Rc by years from 2001 to 2011 that this application covers is negligible therefore the Rc dataset of year 2006 is used as typical values. Accuracy of this application was verified by comparing with JISCARD EX [5].

[1] ICRP Publication 103 (2007)

[2] T. Sato, H. Yasuda, K. Niita, A. Endo and L. Sihver, "Development of PARMA: PHITS-based analytical radiation model in the atmosphere", *Radiat. Res.* 170, 244-259 (2008)

[3] Bartol Research Institute, University of Delaware, Neutron Monitor Data http://neutronm.bartol.udel.edu/~pyle/bri_table.html (Accessed July 2009)

[4] Laurent Desorgher, web site of Physikalisches Institut, Universität Bern, http://cosray.unibe.ch/~laurent/magnetocosmics/ (Accessed July 2009)

[5] H. Yasuda, T. Sato and M. Terakado, "A Personal Use Program for Calculation of Aviation Route Doses", Proc. IRPA12, ID3037:1-4 (2008)

EXPANDING THE PIPELINE - NUCLEAR SCIENCE EDUCATION FOR THE 21ST CENTURY

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These are indeed challenging times for the field of nuclear science - including radiochemistry. With many of the prominent researchers in the field nearing or past retirement age, many departments and universities that once had vibrant programs are choosing to replace the retiring faculty with those in other disciplines. Unfortunately, the engines of research are driven by dollars and the fields of radiochemistry and nuclear chemistry have not been well funded over the recent years. The challenge is how to reinvigorate the field so that new faculty are hired and the future educational and research needs of the country are met. I see funding as a crucial component of this effort. There has been renewed student interest in the general field of nuclear and radiochemistry. We need to match this interest with research programs that provide a funding base for expanded activities. There have been several programs that provide fellowships for graduate education, but this is not the ultimate answer. There needs to be basic research funding to create university-based programs with a visibility that will enable new faculty hires. I will outline some of the directions that we are taking at Maryland to address this challenge and offer suggestions to foster new ties to expand the reach and visibility of nuclear and radiochemistry.

22-S1-2 18331

ACADEMIC RADIOCHEMISTRY PROGRAM IN A CHEMISTRY DEPARTMENT: THE EXPERIENCE AT WASHINGTON STATE UNIVERSITY

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Washington State University (WSU) has had a history of radiochemistry as a component of its chemistry curriculum. Although the program contracted significantly in the 1980’s and 1990’s, a renaissance began around 2002 and continues today due to essential investments from both federal agencies and the state of Washington. These investments have resulted in new faculty additions, and WSU now has a core of seven radiochemistry faculty members within its Chemistry Department of 25 faculty members. These faculty members pursue research in areas such as environmental radiochemistry, chemistry of nuclear fuel cycles, radiopharmaceutical chemistry, actinide computational chemistry, and chemistry of actinide materials while also contributing to a broad spectrum of graduate and undergraduate courses in nuclear and radiochemistry. Unique facilities on campus and strong relationships with Department of Energy national laboratories contribute to the diversity of the program. A brief history of the program will be described, along with the activities conducted in the late 1990’s that led to the reinvigoration at the beginning of this decade. Strategies for sustaining the program and encouraging continued support by federal and state entities will also be described.

22-S1-3 14045

RADIOCHEMISTRY TRAINING AT THE UNIVERSITY OF MISSOURI: A PROGRAM WITH A LONG HALF-LIFE

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The number of chemists who embark on careers in nuclear chemistry, radiochemistry, organic and inorganic radiotracer synthesis, and related disciplines has been a matter of concern for many decades. In 1981, a Committee on Training of Nuclear and Radiochemists was formed from the American Chemical Society Division of Nuclear Chemistry and Technology (DNCT). In 1984, the Committee established a DNCT Summer School in Nuclear Chemistry. In the DOE funded summer school, typically twelve sophomores or juniors are exposed to an intensive six-week period of instruction. In 1989, at the request of the DOE, a second Summer School was established. This program has proven very successful in attracting excellent students to the fields of nuclear and radiochemistry. *It does not, however, address the problems of formal graduate and post-graduate education in this area*. Additional reports published from 1988 – 2007 maintain that the demand for trained radiochemists far outweighs the supply. In 2007 the National Academies and the National Research Council reported that there is an acute shortage of chemists in nuclear medicine and that although the United States still leads chemical research worldwide, its dominance in radiochemistry is being challenged.

The Department of Chemistry at the University of Missouri is committed to a strong radiochemistry graduate training program. A key centerpiece of the radiochemistry program is the University of Missouri Research Reactor Center (MURR), which is the largest research reactor at 10 MW on a University campus. A cyclotron was added in 2008 to the center, which adds charged particle reaction capabilities. The Chemistry Department has a long track record in training Ph.D. chemists and postdoctoral fellows with skills in radiochemistry coupled with synthetic chemistry (organic and inorganic), analytical and environmental chemistry or aspects of biochemistry. The Chemistry Department currently has about 115 graduate students, of which 19 are pursuing their research in the radiochemistry area. We successfully recruit graduate students with interest in radiochemistry primarily from the ACS/DOE sponsored Summer Schools in Nuclear Chemistry. The Department of Chemistry at the University of Missouri in Columbia currently has four radiochemistry faculty members and many skilled radiochemists among different departments on campus. Each brings a different perspective (inorganic, organic, analytical) for the applications of radioactivity. This provides a "critical mass" for addressing multi-disciplinary projects and gives students the opportunity to be exposed to many facets of radiochemistry and nuclear chemistry research. Current applications include those in radiopharmaceutical chemistry, radioanalytical chemistry, radioenvironmental chemistry, archeometry and the preparation of nuclear batteries. Currently, we have established funding from the National Institutes of Health for a T32 training grant and new funding from the Department of Energy for a combined teaching/research grant award in radiotracer applications in biological systems. An overview or the research and education programs in radiochemistry at the University of Missouri-Columbia will be presented.

22-S1-4 21124

RADIOCHEMISTRY EDUCATION AT THE UNIVERSITY OF NEVADA LAS VEGAS

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There is a clear and recognized need for strengthening and enhancing the education of radiochemists in the United States. The radiochemistry program at the University of Nevada Las Vegas addresses this need by educating and training the next generation of radiochemists. The program is unique within the U.S. in so far that it was founded jointly by the chemistry and health physics department at UNLV and resides within the graduate college instead of a single department. The first class of students was accepted in 2004 and since then three students have graduated with a Ph.D. in radiochemistry.

The program focuses on teaching a broad curriculum in traditional and modern radiochemistry and on providing students with the necessary skills to work with radioactive material. This hands-on approach is exemplified in a strong emphasis on student research as well as the large number of experiments taught in laboratory courses. The organization of the program will be described briefly and lessons from the successful operation of the program will be discussed.

A MULTIDISCIPLINARY TEACHING AND RESEARCH APPROACH: ENVIRONMENTAL RADIOCHEMSITRY AT CLEMSON UNIVERSITY

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In 2000, the Nuclear Environmental Engineering and Earth Sciences (NEES) program began a teaching and research track focusing on environmental radiochemistry. The NEES program is housed within the department of Environmental Engineering and Earth Sciences (EE&ES) at Clemson University. The environmental radiochemistry program is designed to introduce students to fundamental concepts such as: understanding chemical behavior and speciation of radionuclides in natural and engineered systems, low-level quantification of radioactivity, and separation and purification of radioactive materials. Students obtain knowledge and training in areas of actinide environmental chemistry, fate and transport of radionuclides in the environment, nuclear waste management, and spent nuclear fuel processing.

In order to develop an environmental radiochemistry program where students will obtain the knowledge and training objectives stated above, a multidisciplinary approach is necessary. Understanding radionuclide behavior in natural and engineered systems is a daunting task which requires understanding of not only fundamental chemical principles and radiochemistry but additional fields such as environmental chemistry/geochemistry, radiation detection and measurement, nuclear engineering, and hydrology. Students within the environmental radiochemistry program take courses in actinide environmental chemistry, environmental health physics, radiation detection and measurements laboratory, and a laboratory course focusing on low level measurements of radioactivity in environmental samples. These courses give students a foundation in nuclear and radiochemistry to build upon. Students take additional courses in various areas such as radioactive waste management, risk assessment, environmental chemistry, geochemistry, surface and subsurface transport, and bioremediation.

The NEES research program follows a similar multidisciplinary approach. Some relevant ongoing research projects which capture this approach are:

Subsurface Transport of Plutonium in Saturated and Unsaturated Subsurface Environments
Radionuclide Sensors for *in situ* Subsurface Water Monitoring
Interactions of Redox Active Radionuclides with Saltstone

Students with a multidisciplinary background in nuclear environmental engineering and science can more fully understand complex, coupled chemical, physical, and biological interactions which will affect radionuclide behavior in natural and engineered systems. Therefore, this educational and research approach will train students and give them the knowledge to join the future nuclear workforce and solve contemporary problems in environmental radiochemistry.

22-S1-6 19291

ON THE NEED OF EDUCATION IN NUCLEAR ENERGY SYSTEMS: PROBLEMS AND CHALLENGES FOR A SMALL UNIVERSITY

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The Finnish universities are obliged to “provide skilled persons for the society” (University Law 645/1997, 4§), the so-called “3rd obligation” – in addition to research and teaching based thereupon. An explicit case is the growing future need for personnel in the existing, as well as the coming, nuclear power plants. This has been clearly pointed out for almost a decade already, but little, if anything, has happened. Today Finland has 4 nuclear plants running, 2 in Olkiluoto (TVO) north of Turku, 2 in Loviisa (Fortum) east of Helsinki, and a fifth is being constructed (in Olkiluoto). Further, several units are being planned by the three energy companies Teollisuuden voima (TVO), Fortum and Fennovoima [1]. The problems related to the teaching of a fairly complicated, many-faceted subject like future nuclear energy systems in a small university like °Abo Akademi are several-fold:

- there is a shortage of personnel if many different subjects are pursued,
- there is an economical shortage since the department has graduation obligations, and
- this leads to concentration in only a few subjects,
- larger companies are unwilling to sponsor, since the unit is ”too small to be effective”,
- there is a shortage of students, since the subject is not (yet) ”in” in the society, etc.

Hence there should be a collaboration between the universities. However, this presents several obstacles. First, the universities that represent teaching or research in nuclear physics are widely spread out, Helsinki (HUT) at 166 km, Jyv¨askyl¨a at 309 km and Lappeenranta (LUT) at 385 km, counted from Turku. Travelwise this is no big problem, but timewise it is, and in addition, external temporal living is expensive. There is a national agreement on study rights at other universities, but those rights are expensive. The presentation reviews the existing courses (prior to 2006). There is an in-house cyclotron, but it is used mainly for medical purposes in conjunction with the Turku PET Centre + Central University Hospital [2]. Further it presents the four new courses developed since, and their contents. Polycopies/compendia written for all of them (as for Nuclear Physics + Laboratory).

Thus, including the Special Assignment and Master’s Thesis, the total volume is presently 101 cp (!) out of a Master’s degree totalling 300 cp.

However, it goes without saying that one cannot do all this alone, and especially the thesis work, being “more technical” benefits from outside supervisor, and at best from power plants!

[1] [www.tvo.fi], [www.fortum.com] and [www.fennovoima.fi], respectively
[2] [www.TurkuPETCentre.fi]

22-S1-7 15197

NUCLEAR KNOWLEDGE MANAGEMENT IN INDIA: PRESENT STATUS AND FUTURE PROJECTION

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India has an active nuclear power program with the mandate:

1) generation of nuclear power to meet energy shortfalls
2) development of newer reactor designs and technologies for utilizing thorium reserves of the country
3) develop advanced technologies for medical and health care, agriculture and industrial applications and spin off benefits.

After the Indo-US 123 agreement nuclear technology and fuel are expected to boost India's nuclear power generations capacity. For the successful gearing up of the program there is need for the nuclear knowledge management which involves:

1) passing on knowledge, skill and expertise from generation to generation
2) generating technically skilled man power on a continuous basis
3) making the program self reliant and self sustaining.

The role of Department of Atomic Energy Commission (DAE) and its affiliates in fostering nuclear technology and nuclear knowledge management is discussed. The present scenario of nuclear field related university education in India is described. Recognizing the exponential growth of energy requirement, the future manpower demand in nuclear industries, reactor technology, and educational and research institutions has been forecasted for the period of 2010 –2025. Technical manpower requirement is estimated deterministically and stochastically based on explicit assumptions about future population growth, dynamics of economic growth, shortfalls in energy requirements and changing pattern of consumption expenditure.

In order to make India self reliant in nuclear science and technology our study suggests the following:

1) recognizing nuclear science/ technology as thrust area at the national area
2) reorganization and augmentation of nuclear education and training programs through universities, institutes and research laboratories
3) global cooperation with international organizations viz. IAEA, World Nuclear University, World Nuclear Association etc. for nuclear knowledge management, academic exchange program, organization of training schools and financial support for research projects
4) special privileges and economic incentives to nuclear science/ technology students
5) development of marketable modules/ study program for requisite nuclear knowledge management

22-S1-8 16760

NUCLEAR FORENSICS SUMMER STUDENT PROGRAM AT LAWRENCE LIVERMORE NATIONAL LABORATORY

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The Lawrence Livermore National Laboratory (LLNL) Nuclear Forensics Summer program is designed to give both undergraduate and graduate students hands-on research opportunities at LLNL for 8-10 weeks during the summer. Approximately 10-15 students conduct research under the supervision of a staff scientist, attend a weekly lecture series, interact with other students, and present their work in poster format at the end of the program.

Currently called the Nuclear Forensics Summer Program, funded out of Department of Homeland Security, this program began 10 years ago as the Actinide Sciences Summer Program. The goal of this program is to facilitate the training of the next generation of nuclear scientists and engineers to solve critical national security problems in the field of nuclear forensics. We select students who are majoring in physics, chemistry, geology/geochemistry, nuclear engineering, chemical engineering and environmental sciences. Students engage in research projects in the disciplines of actinide and radiochemistry, isotopic analysis, radiation detection, and nuclear engineering in order to strengthen the ‘pipeline’ for future hires in the scientific disciplines.

Students are invited to return for a second year at their mentors’ discretion. For the top graduate students in our program, we encourage the continuation of research collaboration between graduate student, faculty advisor and laboratory scientists. These collaborations create a successful pipeline of top quality students from universities across the U.S. Since 2002, 20 summer students have continued to conduct their graduate research at LLNL, 4 have become postdoctoral fellows, and 7 have been hired as career scientists.

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22-S1-9 18929

THE AMERICAN CHEMICAL SOCIETY/DEPARTMENT OF ENERGY NUCLEAR SUMMER SCHOOL PROGRAM

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The Nuclear and Radiochemistry Summer Schools at San José State University and Brookhaven National Laboratory sponsored by the American Chemical Society Division of Nuclear Chemistry and Technology and the U. S. Department of Energy have been held for 26 and 20 years, respectively. During this time, nearly 550 undergraduate students have participated in the intensive six week programs. Recruitment for the programs has been primarily accomplished by student/student contact, faculty recommendation, and by the internet site. The program consists of lectures and hands-on laboratories handling radionuclides. The program brings in outside speakers who meet and have personal contact with the students. A brief review of the lecture topics and the laboratory experiments will be presented.

A survey of the demographics of the participants in the program will be given and compared to the membership of the Division of Nuclear Chemistry and Technology. This data will give a good picture of the state of nuclear and radiochemistry education in the United States.

22-S1-10 13645

NEW INTEGRATED EFFORTS IN UNIVERSITY PROGRAMS TO SUPPORT RADIOCHEMISTRY WORKFORCE DEVELOPMENT

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The U.S. Departments of Homeland Security, Energy and Defense have introduced university programs designed to provide the U.S. national laboratories with a highly qualified workforce in nuclear forensics. These multi-agency integrated programs are designed to recruit the best and brightest students, develop university-based research activities, and to establish collaborative efforts between national laboratories and universities.

The two programs that were implemented during 2008-09 academic year included a graduate fellowship and an award program designed to fit the particular needs of its university applicant. A nationally competitive graduate fellowship program in nuclear forensics made its first eight awards effective on September 1, 2008. This program provides four-year doctoral-degree appointments that include a monthly stipend, full payment of tuition and fees, internship(s) at national laboratories, and required post-graduate positions in nuclear forensics. The program also has an established policy of requiring universities to meet specified criteria prior to being allowed to accept fellowship students. The second program is known as the Nuclear Forensics Education Award program. This broad-based program is encouraging universities to expand their capabilities in radiochemistry and nuclear forensics. This includes funds for instrumentation and equipment, support for faculty members and students, and funds to expand curriculum.

The presentation and complete paper submission will include details on each program and will provide a comprehensive review on the technical areas specifically affected by this program. An area of particular emphasis will be in the development of radiochemistry capabilities as it relates to nuclear forensics at the nation’s universities and national laboratories.

ABSTRACTS: Poster Sessions

PO-1-2-1 18319

FUNDAMENTAL LOW ENERGY NUCLEAR SCIENCE RESEARCH FOR NUCLEAR FORENSICS: PRODUCING AMERICIUM-240

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Due to its role in nuclear forensics and stockpile stewardship science, it is desirable to experimentally measure the neutron-induced fission cross section of americium-240. Such measurements can be performed with as little as 20-100 nanograms using the Los Alamos National Laboratory's Lead Slowing Down Spectrometer. However, because of americium-240's 50.8 hour half-life, it is difficult to produce in these quantities. Work has been done to investigate a new production reaction for americium-240 that involves the bombarding of plutonium-242 with protons at an energy that maximizes the evaporation of three neutrons. This reaction has not been experimentally investigated previously, but has the high predicted production cross section for americium-240 of 100-300 millibarns [1,2].

Targets for the investigation of this nuclear reaction are produced using the molecular deposition cell shown in Image 1, left. The foils are then wrapped in protective catcher foils to prevent the contamination of the beam-line and clamped to a water-cooled metal block. This block is then attached to an electrically isolated irradiation apparatus at the end of a beam-line of the 88-Inch Cyclotron at Lawrence Berkeley National Laboratory. The beam intensity can be measured directly by measuring the current flowing off of the metal beam stop as well as through the use of nickel and titanium proton-monitor foils.

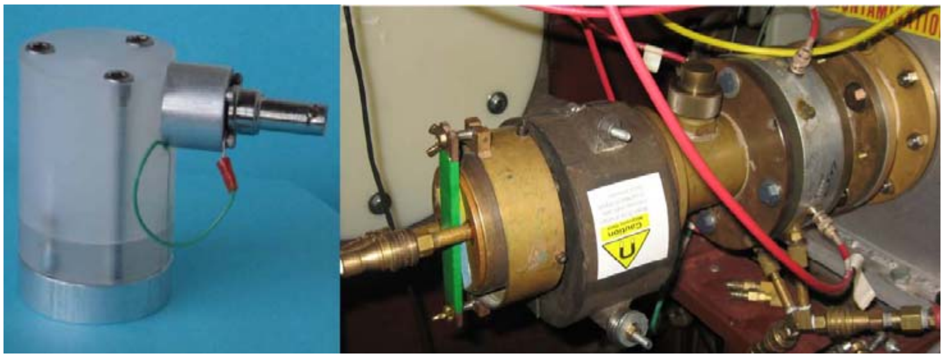

Image 1. Left: the molecular deposition cell used to create the plutonium targets. Right: the irradiation apparatus attached to a beamline at the 88-Inch Cyclotron.

Over the past year, major improvements have been made to the experimental apparatus and procedures for studying this nuclear reaction. Improvements have been made to the process of producing the plutonium-242 targets for irradiation. Also, several improvements are being made to the irradiation apparatus to allow for more safe and reliable cross section measurements of these targets to be made. Upon the completion of several irradiations planned for Fall 2009, we will be able to assess the feasibility of producing americium-240 on the 100 nanogram scale using this new nuclear reaction.

[1] Mashnik, S.G., et al., LANL Report LA-UR-05-7321, Los Alamos (2005).
[2] Mashnik, S.G., et al., Research Note X-3-RN(U)-07-03, LANL Report LA-UR-06-8652, Los Alamos (2006).

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PO-1-2-2 21698

CHEMICAL CONSIDERATION OF RADIONUCLIDES LEAKAGE FROM UNDERGROUND NUCLEAR TESTS

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On-Site Inspection (OSI) is a key component of the verification regime for the Comprehensive Nuclear-Test-Ban Treaty (CTBT). Measurement of relevant radionuclide isotopes created by an underground test (UGT) are the most valuable signatures indicating a nuclear explosion occurred. To prepare for future OSI activity, one must understand which radionuclides are likely to be available for sampling and measurement. Selection of isotopes can be made based on typical nuclear physics parameters: half-life, fission yield, activation cross sections, gamma-ray emission probabilities, and other factors. However, chemical behavior of the radionuclides created in the UGT may have a strong influence in determining what will be available for an OSI measurement.

This is scenario dependant: if a gross vent of radionuclides occurs, some elements that are not very volatile will be transported to the accessible environment. However, the case of slow post-test seepage will be heavily dependant on chemical considerations. For instance, decay chains with noble gas precursors are more likely to transport to the surface. In addition, reactivity of the elements will play a part. Based on an evaluation of chemical behavior, a list of ranked isotopes will be discussed.

^{230}Th-^{234}U MODEL AGES OF SOME URANIUM STANDARD REFERENCE MATERIALS

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The "age" of a sample of uranium is an important aspect of a nuclear forensic investigation and of the attribution of the material to a source. The ^{230}Th-^{234}U chronometer can be used to determine the production date of even very recently-produced material (^{234}U half life = 245,250 ± 490 years; ^{230}Th half life = 75,690 ± 230 years [1]), provided that the ^{230}Th/^{234}U at the time of formation is known, and that there has been no Th-U fractionation in the sample since production. For most samples of uranium, ages determined with this chronometer are "model ages", because they are based on the assumptions of: a) some initial amount of ^{230}Th in the sample, and, b) closed-system behavior of the sample since production. The uranium standard reference materials originally prepared and distributed by the former US National Bureau of Standards and now distributed by New Brunswick Laboratory as certified reference materials (NBS SRM = NBL CRM) are good candidates for materials where these assumptions may be tested. The U isotopic standards have known purification and production dates and closed-system behavior in the solid form (U_3O_8) may be reliably assumed. In addition, these materials are widely available and can serve as informal round-robin inter-laboratory comparison samples.

We determined ^{230}Th-^{234}U model ages for seven of these isotopic standards by isotope dilution mass spectrometry using a multi-collector ICP-MS. The standards dated for this study are: U005-A, U010, U030-A, U100, U850, U900 and U970. Model ages obtained range from ~30 to ~52 years ago (reference date: 5-May-2009). For six of the seven standards analyzed, the model ages are older than the purification dates of record. The model age of U100 is the same as the purification date, within uncertainty. For the other six standards analyzed, the magnitude of the discrepancy between model age and purification date does not correlate with the model age or the amount of ^{232}Th in the samples. This indicates that excess ^{230}Th in the standards results from incomplete purification during production of the standard.

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PO-1-2-4 20021

DEVELOPMENT OF RESONANCE IONIZATION MASS SPECTROMETRY FOR MEASURING URANIUM ISOTOPE RATIOS IN NUCLEAR MATERIALS

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Isotope abundances of the actinides, particularly uranium, are of primary importance in nuclear forensic investigations. Current approaches to measuring the isotope ratios of the actinides in nuclear materials rely on time-consuming dissolution and chemical separations. Resonance Ionization Mass Spectrometry (RIMS) is capable of measuring these isotope ratios rapidly and with high sensitivity, significantly reducing the time between sample receipt and first analytical results. We demonstrate a new approach, capable of measuring U isotope ratios to better than 1% directly from uranium oxides without any sample preparation, aside from mounting for analysis. For our studies we used the CHARISMA instrument at Argonne National Laboratory [1]. In CHARISMA, measurements are performed directly on solid materials by ion sputtering (25 keV GA^+) or laser desorption (third-harmonic Nd:YAG), producing a cloud of desorbed material. An electric potential is applied, sweeping charged particles away. The remaining neutral atoms and molecules are irradiated by lasers tuned to excite a series of specific states in the element or isotope of interest leading to preferential ionization of the target species. The ionized atoms are then accelerated into a time-of-flight mass spectrometer for measurement. The unique approach of RIMS, providing selective ionization of the element of interest, eliminates isobaric interferences and obviates the need for chemical separation. Resonance ionization of uranium for isotopic ratio measurements can be problematic because of large splitting in the atomic energy levels of the various isotopes, e.g., 7 pm between ^{235}U and ^{238}U in the resonance of interest. We avoid fractionation in the ionization of U by broadening the bandwidth of the laser used in the first resonance step to be larger than the isotope shift itself, i.e., increasing bandwidth from 2 pm to 10 pm. We report progress on high precision (0.5%) measurements of isotope ratios of U directly from U3O8 utilizing a 3-color, 3-photon scheme adapted from Schumann *et al.*, 2005 [2]. Three adjustable laser parameters – wavelength, power, and bandwidth – dominate the response of desorbed atoms to the applied laser fields in RIMS. By studying the effects of each of these parameters we have begun to build a systematic understanding of isotope fractionation and reproducibility in uranium due to ionization by particular laser configurations. The immediate result has been the development of more robust, effective ionization schemes. Measurements have been successful using both UO_2 and U_3O_8 standards, with no sample treatment or preparation prior to analysis. Both major (^{235}U, ^{238}U) and minor (^{234}U, ^{236}U) isotopes are clearly distinguished in our data with no interferences.

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APPLICATION OF RESONANCE IONIZATION MASS SPECTROMETRY TO DETECTION OF URANIUM IN NATURAL SILICATE MATRICES

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Rapid characterization of actinide isotopic compositions in silica-dominated materials is essential to the investigation of debris and environmental samples. We have developed Resonance Ionization Mass Spectrometry (RIMS) methods aimed at optimizing uranium isotope analyses of solid materials. RIMS couples multiple laser beams tuned to element-specific excited electronic states to selectively ionize elements of interest while suppressing isobars. While developmental work has focused on uranium oxides (Isselhardt *et al.*, this volume), we have also begun to apply RIMS to rapid uranium isotopic determination in silicate and glass matrices. Analysis of actinides in silicates is of interest to the interrogation of environmental samples as well as melts or condensates potentially found in nuclear fallout. Previous RIMS studies have shown substantial reduction in U sensitivity when analyzing elements in amorphous materials. Our goal is to explore the optimal conditions for and limitations to the detection of uranium from silica-dominated matrices.

Initial studies have focused on natural silicate ores such as cuprosklowdowskite (hydrated copper uranyl silicate). Mineral fragments were mounted in resin, polished with ~6 um diamond, and imaged by backscattered scanning electron microscopy to characterize mineral heterogeneity. Experiments were conducted on the CHARISMA instrument at Argonne National Laboratory (Savina *et al.*, 2003). We desorbed neutral uranium atoms and molecules from the samples using two ablation methods: a focused third harmonic Nd:YAG laser beam, and a 25 keV Ga^+ ion beam. Uranium was resonantly excited and ionized via a 3-color laser scheme (after Schumann *et al.,* 2005). Uranium has large ground state isotope splitting, as much a 7 pm between the ^{238}U and ^{235}U at the resonances of interest. To avoid isotopic fractionation due to small shifts in laser wavelength, we broadened our laser bandwidths for the first and second resonance steps to ~15 pm.

We achieved significant U ion yield in analyses of complex natural U-bearing silicates using both laser and ion beam desorption. Quantification of relative atomic U and molecular UO and UO2 yields is underway. Off-resonance spectra, with the first laser tuned 200 pm off resonance to longer wavelength, resulted in the generation of molecular ions but no U ion signal. Despite the diversity of elements present in the cuprosklowdowskite sample, ionization of other elements and their compounds was quantitatively suppressed. Future work will include comparative studies of uranium RIMS from other silicate minerals, as well as uranium-doped glasses. The effects of the silicate and glass matrices on neutral atom yields, and optimal analytical conditions for U isotopic measurements from such matrices have not yet been fully evaluated.

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RECENT IMPROVEMENTS TO THE ENVIRONMENTAL SAFEGUARDS ANALYSIS PROGRAM AT LOS ALAMOS

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As a member of the Network of World Analytical Laboratories (NWAL), Los Alamos National Laboratory (LANL) is responsible for the analysis of environmental safeguards samples collected by the International Atomic Energy Agency (IAEA). These samples are collected in safeguarded nuclear facilities around the world under the 93-2 Additional Protocol agreement that is part of the Nonproliferation Treaty (NPT), and distributed to NWAL laboratories for analysis of fission products, actinide concentrations, and actinide isotopic compositions. A number of changes and improvements to our analytical protocols at LANL have been implemented to address some of the unique challenges associated with these samples. Because of the extremely large dynamic range of uranium and plutonium concentrations in these samples (7 orders of magnitude), rigorous screening and sample processing protocols have been implemented to prevent laboratory contamination and sample-to-sample cross contamination. Improvements include using a Compton-suppressed gamma-ray spectrometer to lower uranium detection limits, setting up multiple ashing and dissolution laboratories for different activity levels, adding an inductively-coupled plasma mass spectrometry (ICP-MS) screening analysis for uranium concentration and isotopic composition, and alpha spectrometry screening analysis for plutonium concentration. Additionally, a study of sample-to-blank cross-contamination and evaluation of the uranium process blank were completed.

PO-1-2-7 15658

QA/QC ACTIVITIES AND ESTIMATION OF UNCERTAINTY FOR ULTRA-TRACE ANALYSIS OF URANIUM AND PLUTONIUM IN SAFEGUARDS ENVIRONMENTAL SAMPLES

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JAEA (Japan Atomic Energy Agency) has been conducting the environmental sample analysis, which is one of the IAEA's safeguards measures. In the analysis, isotope ratios of ultra-trace amounts of nuclear materials (uranium and plutonium) in samples taken from nuclear facilities are determined to detect 'environmental signature' of undeclared nuclear materials and activities. In order to keep and enhance the reliability of the measurement results, validation of analytical methods and estimation of measurement uncertainty in such ultra-trace analysis should be properly done in accordance with worldwide standards. In this presentation, the authors introduce current activities on achievement of QA/QC (quality assurance and quality control) and estimation of measurement uncertainty in the ultra-trace analysis at CLEAR (Clean Laboratory for Environmental Analysis and Research) of JAEA.

PHYSICAL PROPERTIES OF OXIDIZED NUCLEAR MATERIALS

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Identifying the physical and chemical properties of special nuclear material (SNM) is important in understanding how SNM material behaves in the environment and how these materials can form powders with different particle size distributions. The particle size distribution is important because it can have significant effects on human health hazards of the materials. The techniques that are applied for the study of the chemical properties of SNM are well known and well developed. The techniques for analyzing the physical properties of SNM need to be applied to a variety of materials to enhance the understanding of how the physical properties are affected by different samples. This paper describes the physical analysis of a variety of SNM oxides including uranium oxide and plutonium oxide powders. The oxide powders are produced under controlled conditions (temperature and humidity) and processing conditions. The analytical techniques applied include gas pycnometry (to determine density), particle size analysis (to analyze the particle size distribution), and microscopy (to determine the morphology and microstructure). The results will demonstrate how an oxide material density, particle size distribution and morphology and microstructural can vary for materials produced under different processing and environmental conditions.

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NUCLEAR FORENSIC INFERENCES USING ITERATIVE MULTIDIMENSIONAL STATISTICS

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Results from a novel chemometric approach to the attribution of nuclear material of unknown or unverified origin by comparison to a global database of commercial uranium ore concentrate samples are presented. Major and trace element, as well as isotopic concentrations were used to build a multivariate classification model which was tested using both internal and external validation. Partial least squares discriminant analysis classification was applied iteratively using a process of elimination to remove low likelihood sources from the model until a conclusive determination could be made. This approach will be demonstrated using real-world materials.

PO-1-2-10 21363

LOCAL AND GLOBAL FALLOUT PRESERVED IN LAKE SEDIMENT FROM THE SIERRA NEVADA, CALIFORNIA

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Cesium-137, plutonium and ^{236}U have been identified in the topmost 10 cm of sediment from Upper Highland Lake in the Sierra Nevada, Alpine County, California. The depth-profile of fallout material in the sediment core was investigated as part of a summer student internship program at LLNL designed to teach laboratory and instrumental techniques for analysis of environmental samples for safeguards and nuclear forensics. Two-centimeter segments of the sediment core were analyzed first by gamma spectrometry and then spiked with ^{233}U and ^{244}Pu tracers and leached in nitric-hydrofluoric acid to extract labile U and Pu from the sediment. The U and Pu were separated from the leachate, purified and analyzed by multi-collector ICPMS (NuPlasma HR) to determine the isotopic compositions and concentrations. With increasing depth, the first four 2-cm increments have ^{240}Pu/^{239}Pu of 0.136, 0.142, 0.156 and 0.113, which are all significantly lower than the accepted average of 0.18 for global fallout, and point to a contribution from atmospheric testing at the Nevada Test Site. In these same increments, the Pu concentration decreases from 3.08 to 0.20 pg/g-dry sediment, and 236U decreases from 1.48×10^9 to 2.8×10^8 atoms/g-dry sediment. These ^{236}U concentrations are similar to those reported by Sakaguchi et al. [1] for soil samples from Japan affected only by global fallout. The ^{236}U/^{239}Pu is 0.26 in the upper 8 cm of our lake sediment core, which, again, is consistent with the estimates for global fallout by Sakaguchi et al.. Our measurements of ^{236}U/^{238}U in the leachate fractions also decrease with depth in the core from 2.12×10^{-7} to 2.8×10^{-8}, while the ^{236}U/^{239}Pu is essentially constant over the first 6 cm indicating lack of significant chemical fractionation between fallout derived uranium and plutonium in this lake.

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PO-1-4-1 20274

STUDY ON SOLVENT CLEANUP USING ACTIVATED ALUMINA FOR PUREX PROCESS

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In the PUREX process, uranium and plutonium are extracted from nitric acid, which contain uranium and plutonium, by solvent extraction. The extractant composes of 30% tributyl phosphate (TBP) and n-dodecane. TBP and n-dodecane are changed into degradation products by radiation and/or nitric acid [1]. Generally, TBP degradation products can be washed by alkali solution like sodium carbonate solution, however, n-dodecane degradation products are not easy to be removed by the above method [2]. Solvent cleanup method using activated alumina was discussed in this study. This method was one of candidate to remove the degradation products from the extractant [3]. The degradation sample of 30% TBP/n-dodecane was prepared by irradiation (1.6MGy) using ^{60}Co gamma-source. The degradation products were qualitatively analyzed by Gas Chromatography -Mass Spectrometer (GC-MS). After the irradiation, solvent cleanup was performed by activated alumina, and a phase separation test with 3MHNO3 was performed for evaluation of the cleanup effect. As the result, it was found that the n-dodecane degradation products were hexane and long-chain alcohols, and almost 70% of the degradation products were removed and the phase separation performance were improved by the cleanup using activated alumina (Table 1).

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PO-1-4-2 21122

ALLOY FORMATION OF ACTINIDES OR LANTHANIDES DURING ELECTROCHEMICAL DEPOSITION IN LICL-KCL EUTECTIC

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Pyrochemical processing of nuclear fuels using a molten salt as a solvent is regarded as one of the promising options for future spent nuclear fuel management.[1-4] Molten salts are known as suitable media for electrorefining and electrowinning of metal.[1-4] In order to reach a better understanding and control of these metal deposition processes, accurate knowledge of the electrochemical deposition mechanism is essential. Therefore, many electrochemical studies of actinides (An) and lanthanides (Ln) in various molten salts have been carried out in the past decade.[1-4] However, the electrochemical reactions of the Pyrochemical processing are not such simple due to a variety of the reactions of Ans and Lns. For example in case of Nd^{3+} and U^{3+} system in LiCl-KCl eutectic melt, electrochemical deposition of Nd takes place at more positive potential than in the system without U^{3+}, which may resulted from a formation of alloys between the elements in the electrochemical baths. In order to investigate and differentiate the complicated electrochemical reactions of Ans and Lns in LiCl-KCl eutectic melt, UCl3 and some Lns are introduced into an electrochemical bath of the molten salt. Electrochemical techniques such as cyclic voltammetry, square wave voltammetry etc. as well as surface analysis techniques such as scanning electron microscope, X-ray diffractometer, etc. were employed to interrogate the reactions. The details of the experimental results and discussion will be presented in the poster session of a conference.

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PO-1-4-3 19735

COMPLEXATION OF Pu(IV) WITH ACETOHYDROXAMIC ACID: SOLVENT EXTRACTION WITH DI(2-ETHYLHEXYL) PHOSPHORIC ACID

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Thermodynamic properties of metal-ligand interactions are important when considering large-scale liquid-liquid separation processes. Stability constants at specific ionic strengths and temperatures are essential for modeling and predicting the speciation of metals through multistage processes such as UREX+. Acetohydroxamic acid (AHA) has been recognized as a salt-free organic compound that has a powerful redox and complexation capability and can selectively strip Np(VI) and Pu(IV) from the uranium-tri-*n*-butyl phosphate extraction product. Although AHA can participate in multiple metalligand equilibria in UREX+, we are particularly interested in plutonium as it is one of the more crucial elements to control in used nuclear fuel reprocessing. Solvent extraction of radiotracer solutions has shown to be an effective method for determining stability constants when concentrations of metals are low and it is particularly useful for investigation of complexation of actinides. The stability constant of the Pu(IV)-acetohydroxamic acid complex ($Pu(AHA)^{3+}$) at 1*M* ionic strength has been investigated by extraction with di(2-ethylhexyl) phosphoric acid (HDEHP). Pu(IV) was extracted from perchloric and nitric acid media at various AHA concentrations. The distribution data confirm a strong Pu(IV) complexation in the aqueous phase and allow for the calculation of the stability constants through graphical methods. The value of β1 obtained by extraction with HDEHP is one order of magnitude above the values obtained by extraction with thenoyl trifluoroacetone (TTA) [1-3], which has a considerable solubility in aqueous solutions [4] and leads to lower metal distribution ratios. The reported value for the first stability constant of the Pu-AHA complex is in excellent agreement with the recent value obtained by absorption spectroscopy [5].

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CHROMATOGRAPHIC PARTITIONING OF A CESIUM FROM SIMULATED HLW USING A MACROPOROUS SILICA-BASED CALIX[4]ARENE IMPREGNATED SUPRAMOLECULAR RECOGNITION COMPOSITE

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Radioactive Cs-135 and Cs-137 with the half-lives of 2×106 and 30 years are the harmful fission products (FPs) contained in highly active liquid waste (HLW). It is well known that Cs-135 has a long-term adverse impact on the environment because of its mobility in final repository. Cs-137 is one of main heat emitting nuclides and is harmful to the vitrifiered HLW. On the other hand, Cs-137 can be used as radiation and heat source. Thus, effective separation and recovery of Cs from HLW are valuable. For this purpose, we prepared a novel macroporous silica-based supramolecular recognition composite containing a calixarene-crown molecule and developed a new separation process of Cs(I) utilizing minimal organic solvent and compact equipment by extraction chromatography.

The novel macroporous silica-based (Calix[4] arene-R14+Oct)/SiO2-P composite was synthesized by impregnating 1,3-[(2,4-diethylheptylethoxy) oxy]-2,4-crown-6-calix[4]arene and octanol molecules into the pores of the macroporous SiO2-P particles. The concentration of the FP elements La(III), Y(III), Mo(VI), Pd(II), Ru(III), Rh(III), Cs(I), and Zr(IV) was 5 mM, respectively. The HNO3 concentration was in the range of 0.3 M to 7.0 M. The separation experiment was performed by the silica-based composite packed column with 10 mm in diameter and 300 mm in length at 298 K. The flow rate was controlled to 1.0 cm3/min. Fig.1 shows the effect of the HNO3 concentration on the tested elements adsorption onto (Calix[4]arene-R14+Oct)/SiO2-P. It was found that in 4 M HNO3 solution, the silica-supramolecular recognition composite had strong adsorption ability and high selectivity for Cs(I) over all of the tested elements. Fig.2 shows the separation behavior of Cs(I) by (Calix[4]arene-R14+Oct)/SiO2-P packed column. With the supplement of feed solution, La(III), Y(III), Mo(VI), Pd(II), Ru(III), Rh(III) and Zr(IV) showed almost no adsorption and were quickly eluted along with 4 M HNO3. As water was supplied to the adsorption column, Cs(I) was efficiently eluted. The elution band observed was narrow and sharp without tailing, reflecting a rapid elution dynamics. The complete separation and recovery of Cs(I) from simulated HLW by the novel macroporous silica-based supramolecular recognition composite have been achieved.

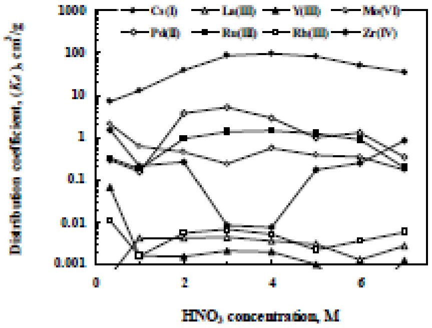

Fig.1 Effect of HNO$_3$ concentration on the adsorption at 298 K

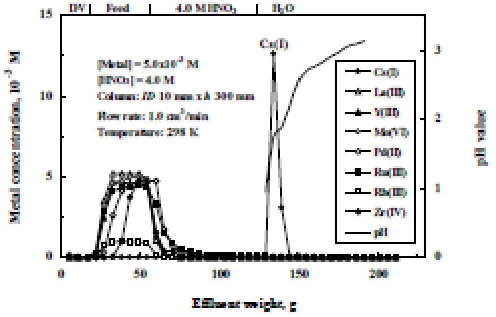

Fig.2 Chromatographic separation performance using (Calix[4]arene-R14+Oct)/SiO$_2$-P.

PO-1-4-5 15567

MONITORING OF SPENT NUCLEAR FUEL REPROCESSING STUDIES BY UV-VISIBLE SPECTROSCOPY

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UV-visible spectroscopy was evaluated as a method for process monitoring and safeguards in the solvent extraction separations of spent nuclear fuel. Specifically the speciation of uranyl in the tributylphosphate-dodecane-nitric acid system was explored as a model for the UREX process. A compact spectrometer and light source were connected to a fiber optic dip probe for real-time monitoring when inserted into process streams. The probe was mounted in a Swagelok fitting in the product stream of a 20-stage, 2-cm contactor bank at ANL. The operation of the fiber optic system was verified by comparing static sample measurements with those from a robust benchtop spectrophotometer. In these comparisons, the 414 nm absorption peak in a 0.113 M uranyl solution in the fiber optic system yielded a maximum absorption of 0.9990 while the benchtop UV-Visible measurement was 1.0505, a 4.9% deviation relative to the latter value. While no peak shifts were present, the fiber optic system displayed noise levels significant enough to wash out any spectra at wavelengths below 360 nm and above 940 nm, well outside the region of interest. Flowing sample experiments, utilizing a diaphragm pump and fiber optic dip probe mounted as in the contactor setup, indicate no change in spectral results across flow rates of 10 to 40 mL/min, and conservative uranium detection limits of 0.0113 to 0.5660 M with a resolution of greater than 0.003 M. Current research focuses on quantifying and optimizing the precision of a cuvette-based flow cell system with peristaltic pump for 0.01-1.26 M $UO2^{2+}$ solutions. The results will be used in conjunction with EXAFS spectroscopy on the uranyl di-and tri-nitrato species in order to produce a defined relationship between the UV-Visible spectra of a uranyl solution and the speciation of the uranium(VI) nitrate species in nitric acid, from which process conditions can be deduced for both uranyl and nitrate concentrations.

DISSOLUTION, AN ESSENTIAL STEP FOR ANALYSIS OF IRRADIATED FUELS AND TARGETS: ATALANTE EXPERIMENTS AND STUDIES

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For mainly characterization of irradiated fuel and targets, the dissolution step can not be circumvent and is determining for the downstream analytical steps. However the objectives to be reached depend on this finality. CEA teams work on these aspects in the Atalante facility. Concerning the chemical and isotopic characterization of irradiated materials, the objective would be clearly a quantitative dissolution in one step of these solids without any loss by volatilization or precipitation of the elements of interest. Very often, the complexity of the matrix retained for its refractory properties and the diversity of chemical behavior of the elements to be analyzed are antagonistic so that the one step concept cannot be applied. In addition, the conditions and the choice of the dissolution mediums must take account of the analysis techniques in terms of impurities and interferences thus total uncertainties aimed. Each case is the subject of a specific study where the dissolution conditions and mediums go from the "simple" mixture of acids to the use of melting salts at temperatures going up to 1000 C. Whatever is the aim of the studies described above; they are associated with theoretical approach based as well on kinetic and thermodynamic methods. This presentation is focused on the experimental steps retained applications detailed for various characterization of irradiated targets and fuels. Several dissolution conditions of oxide fuels will be described associated with some analytical results about gaseous nuclides. About target characterizations, two examples will be taken about in Phenix fast neutron reactor irradiations. The first one will describe the remote handling and dissolution of pure isotopes in the scope of cross section measurements and the second the dissolution of AmO2-MgO targets in the scope of Ecrix americium transmutation program. After analysis of resulting solutions, experimental results are used for evolution calculations in nuclear reactors.

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RADIONUCLIDE SORPTION ON GRANITIC MATERIAL: EFFECT OF THE BET SURFACE AREA AND PARTICLE SIZE

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Storage of spent nuclear fuel in a deep underground repository is an option chosen by many countries using nuclear power. In the case of a failed repository, the host rock would ultimately be the final barrier between the radiotoxic waste and the biosphere, and sorption reactions could substantially decrease the radionuclide transport. In safety analysis for the final repository, the retention properties of the rock are therefore essential. The radionuclide retention properties of the rock material are commonly determined in small scale experiments, using crushed geological material. To obtain sorption quantifications for the intact material, the experimental results for small particles are sometimes up-scaled by extrapolation to infinite particle size, assuming a linear relationship between sorption and the specific surface area, or the inverse of the particle size. However, this approach has been found to overestimate the radionuclide retention properties of granitic material (André et al., 2008, 2009). This work aims at studying and establishing the relationships between the specific surface area, the particles size and the sorption for pure mineral phases. In a first step, the surface area is determined by the BET method for different particle size of some pure minerals representing the most common minerals composing granitic rock, such as chlorite, quartz, labradorite, K-feldspar, magnetite, pyrite, calcite or apatite. Special focus is on the extrapolation of results from crushed material to the intact material and comparison to the experimentally determined BET area for large mineral pieces. In a second step, the relation found between mineral surface and particle size is used, together with literature sorption data, to construct a predictive model of the surface area dependence of the Ni^{2+} and Cs^{+} sorption strength for the investigated minerals.

André M., Malmström M. E., Neretnieks I. (2008) Measuring sorption coefficients and BET surface areas on intact drillcore and crushed granite samples, *Radiochimica Acta* **96**(9-11): 673-677.
André, M., Malmström, M. E. & Neretnieks, I. (2009) Specific surface area measurements on intact drillcores and evaluation of extrapolations methods for rock matrix surfaces. (In print).

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THE RESULTS OF FUEL LEAK TESTS AT UNIT 4 OF PAKS NUCLEAR POWER PLANT

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Background: Quite a high iodine activity was observed just after the restart of Unit 4 in 2008. The ^{131}I activity values exceeded the values of the first control level specified in the Technical Specifications; the total iodine activity approached the relevant first control level. This high level lingered for several days and did not rise further. During the campaign, it stabilised after a slow decrease, but stayed at a level, which was higher than that of the previous campaigns, and that of the other Units. The increase and the nature of the activity referred to fuel failure. The increase of iodine activity did not require Unit shutdown, and a decision was made to find the failed fuel assembly during the maintenance outage in 2009.
Procedure: A Höfer & Bechtel telescopic sipping device, which has been available in the power plant since autumn 2008, was used during the refuelling work at the end of the campaign, to identify the failed fuel assembly. This method consists of the lifting of each fuel assembly, causing the external hydraulic pressure to decrease, as a result of which the damaged rods are expanded, and the accumulated radioactive material vented. This was the first time such device was used during re-fuelling straight after the shutdown of the reactor. The processing of the first test results provided important information about the operation of the sipping device, and for the possible application this device in the future. The calculation procedure, developed earlier for modelling the sipping process can be corrected with the use of the information available. Results: After shutdown of Unit 4, a sipping test was carried out for each fuel assembly. During the test, each fuel assembly was raised by the Refuelling Machine, and the activity of the gas, which was recovered from the water pumped through the fuel assembly, was continuously measured with the use of a scintillation detector and the sample of water was laboratory analysed for composition. The water in the refuelling pool was sampled every day for laboratory analysis and for tracing the test backgrounds. Conclusions: The failed fuel, which became leaking probably due to manufacturing error and caused a significant increase of activity during the Campaign 22 of Unit 4, was successfully identified with the use of the telescopic sipping device. The measurement results obtained showed a several order of magnitude increase in activity as compared to the background and thus positively identified the fuel assembly containing the defective rod.

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AMBERLITE XAD-2 IMPREGNATED CYANEX272: SORPTION DESORPTION STUDIES OF Th(IV)

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Amberlite XAD-2 impregnated with Cyanex272 was packed in a column and studied for sorption desorption of Th(IV). The influence of various parameters like acid concentration, aqueous phase flow rate, nature and concentration of eluents and other ions were systematically studied. Th(IV) was quantitatively sorbed from 0.001 M HNO3. It was recovered using 10cm^{3} of 4M HCl at 0.6 cm^{3} min^{-1} flow rate. Batch method was used to understand adsorption behavior of Th(IV) using Langmuir and Freundlich adsorption isotherm models. The sorption capacity of the impregnated resin for Th(IV) was 8.48 mmol/g. The limit of detection for Th(IV) was 0.67 μg dm^{-3} and a reusability for more than 65 cycles was observed. The method developed applied for isolation of Th(IV) from monazite sand was reproducible with a relative standard deviation (R. S. D.) of 0.8 %. *Keywords*: Amberlite XAD-2, Cyanex272, Th(IV), sorption, monazite sand.

PO-1-4-10 15975

KINETICS STUDY ON MIGRATION PROCESSES OF ENERGETIC DEUTERIUM IMPLANTED INTO BORON FILMS

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As to the fusion reactor development, knowledge on high energy chemical behavior of energetic hydrogen isotopes, especially escaped ones from fusion plasma, in plasma-facing materials such as the first wall and diverter has been required increasingly. In the first walls of fusion reactors, boronization is considered to be one of the most useful wall conditioning techniques for the reduction of impurities in plasma. The first wall will be exposed to some energetic particles including tritium, therefore, it is important from tritium safety point of view for fusion reactors to elucidate the chemical behavior of energetic hydrogen isotope implanted into boron coating film. It has reported that B-D and B-D-B bonds are formed in the pure boron coating films after $\mathrm{D2}^+$ ion implantation [1]. However, studies on dynamics of hydrogen isotopes in boron coating films have been limited so far. In the present study, it was purposed to understand the kinetics of deuterium desorption process; the depth profile of deuterium implanted into the pure boron coating film was evaluated by secondary ion mass spectroscopy (SIMS) with heating samples at various temperatures, and it was analyzed by means of the mass balance equation. The pure boron coating film was deposited on a silicon substrate by a plasma chemical vapor deposition method and its characterization was performed by X-ray photoelectron spectroscopy (XPS). After preheating treatment, 1 keV $\mathrm{D2}^+$ ions were implanted into the boron coating film with the flux of 1.0×10^{18} m^{-2} s^{-1}, the fluence of 1.0×10^{22} m^{-2}, and depth profile was measured by SIMS. The sample was heated isochronally or isothermally, and the depth profiles of deuterium were measured after heating treatments. It was observed by SIMS that implanted deuterium ions were retained in the depth of 24 nm from the surface and it was migrated toward the surface by heating. In isochronal experiments, it was indicated that the rate-determining step of the deuterium desorption process in pure boron film was changed from diffusion process to the recombination reaction. Furthermore, on isothermal experiments, the recombination rate was determined by the mass balance equation [2] from the concentration of the largest deuterium existing area, it's the depth at there and FWHM, and activation energy of recombination was also calculated. Using these results, simulation of tritium migration process taking account of the isotope effects in boron films will be discussed in the present paper.

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THE SPECIATION AND SOLUBILITY OF AMERICIUM IN BEISHAN GROUNDWATER

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The speciation and solubilities of transuranic elements in the groundwater of a potential geologic repository are important for the pre-safety assessment of the repository. In this study, the speciation and solubility of americium in Beishan groundwater (pH=7.25) are calculated by CHEMSPEC. Beishan area in Gansu Province, in the Northwest of China, has been selected as an important research area for China's potential geologic repository. CHEMSPEC is a speciation analysis code based on the mass balance algorithm developed by the Peking University. The calculated solubility of americium in Beishan groundwater is 2.9×10^{-7} mol/L. The solid phase is $AmOHCO_3$ and the major aqueous specie in groundwater is $AmCO_3^+$ in the original groundwater condition. The influence of pH and total carbonate concentration on the solubility is also studied. The pH range is 6~10 and 2 total carbonate concentrations are considered (1×10^{-2}, 1×10^{-4} mol/L). Fig. 1 shows the calculated results. The solubility of americium in Beishan groundwater decreases as the pH increases. When the total carbonate concentration is 1×10^{-4} mol/L, the solid phases are $AmOHCO_3$ ($pH \leq 8$) and $Am(OH)_3$ ($pH \geq 9$). While when the total carbonate concentration is 1×10^{-2} mol/L, the solid phases are $Am_2(CO_3)_2$ ($pH \leq 6$) $AmOHCO_3$ ($7 \leq pH \leq 9$) and $Am(OH)_3$ ($pH \geq 10$). The solubility range of americium in Beishan groundwater is 4.2×10^{-4}~ 1.5×10^{-10} mol/L.

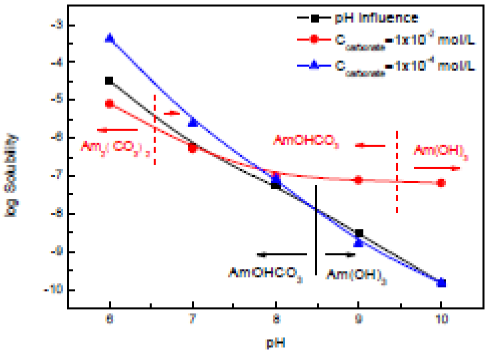

Fig. 1: The influence of pH and total carbonate concentration on solubility of americium in Beishan groundwater calculated by CHEMSPEC

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COBALT BIS(DICARBOLLIDE) ION DERIVATIVES COVALENTLY BONDED WITH DIGLYCOLYLDIAMIDE FOR LANTHANIDE AND ACTINIDE EXTRACTION

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Spent nuclear fuel produces high-active liquid waste. One of the possibilities how to reduce amount and toxicity of the spent nuclear waste is the reprocessing consisting of separation of the most dangerous radionuclides, particularly minor actinides (^{241,243}Am, ^{245}Cm, ^{237}Np) responsible for the long-term radiotoxicity of the waste. Several hydrometallurgical process based on use of different extractants have been designed during the last decades for reprocessing. Between them, amide-type extractants, e.g., diamides as *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) were proposed for efficient group extraction of actinides/ lanthanides from the nuclear spent (e.g. "ARTIST" process [1]). In our work we have been aimed in desing of extraction agents containing cobalt bis(dicarbollide) ion(1-), [(1,2-C2B9H11)2-3-Co]$^-$ (COSAN) in a single molecule to improve extraction efficiency and minimize generation of the secondary waste. The COSAN is singly charged (1-) strongly hydrophobic anion that belongs to the class of electron deficient 26-electron 12-vertex icosahedral *closo* borane cluster family, known for its extraordinary high chemical and thermal stability, hydrophobicity and inorganic super acid behavior. Recently carried out research has shown, that covalent bonding of COSAN with *N,N*-alkyl carbamoylmethyl-dialkylphosphine oxides – (CMPO) chelating groups into a single molecule significantly improves the extraction efficiency in comparison with “classical” metal ligands or their synergic mixtures with halogenated COSANs [2]. In this contribution, we report on new class of extractants based on two COSAN anions covalently bound to organic, diglycolyl acid platform by amidic bonds. The series of newly prepared derivatives of COSANs with diglycolyldiamide substituents [3] differ in substitution on amide nitrogens and the mode of attachment of the two COSAN anions. The compounds were tested for extraction of lanthanides and actinides from fission product mixture from PUREX feed. We found, the covalent combination of ionic COSAN with chelating groups in TODGA-like compounds proved similar positive effect on the extraction efficiency [3]. The most efficient group of such compounds presented here consists of compounds with long, diethyleneglycol connectors between COSAN cage and diglycolamide group. These derivatives differ in substituents on amidic nitrogen atom (by butyl-, octyl-, *terc*-octyl-, dodecyl-, benzyl-). The influence of the substituents as well as effect of diluents, composition of aqueous phase on the extraction efficiency for trivalent radionuclides will be presented.

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[1] See for example: Extraction of Actinides Using N,N,N",N'-tetraoctyl Diglycolamide (TODGA): a Thermodynamic Study. S. A. Ansari, P. N. Pathak, M. Husain, A. K. Prasad, V. S. Parmar, and V. K. Manchanda, *Radiochim. Acta*, **94**, 307-312 (2006) and the references therein.

[2]See for example: Lanthanide and Actinide Extractions with Anionic Ligands Based on Cobalt Bis(dirabollide) Ions with Covalently Bonded CMPO Functions. P. Selucký, J. Rais, M. Lučaníková, Grüner, M. Kvíčalová, K. Fejfarová, and I. Císařová, *Radiochim. Acta* **96,** 273-284 (2008) and the references therein.

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J. Organomet. Chem., submitted.

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PARTITIONING AND TRANSMUTATION – INTERNATIONAL SCENARIO

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The high level waste (HLW) generated during spent fuel reprocessing contains unextracted U, Pu alongwith bulk of minor actinides such as Am, Np, Cm and host of fission products like Tc, Pd, I, Zr, Cs, Sr and lanthanides as well as activation products. At present, the most accepted approach for the management of HLW is to vitrify it in the glass matrix followed by it's interim storage for ~50 years (to allow for the decay of ^{137}Cs and ^{90}Sr) and it's future disposal in deep geological repositories . Since the half-lives of minor actinides and some of the fission products range between few hundreds to millions of years, the concept of surveillance of vitrified HLW in geological repositories over such long periods is debatable from economical as well as environmental safety considerations particularly due to the distinct possibility of the migration of long lived alpha emitting minor actinides in the aquatic environment. There is growing consensus internationally to address the issue through P&T (Partitioning of long-lived radionuclides followed by Transmutation) strategy. It envisages the complete removal of minor actinides from HLW (<4000 Bq/gm) and their subsequent incineration (as suitable targets) in the fast flux reactors / accelerators. This approach is likely to reduce the need of geological repositories significantly and in addition it works as an energy amplifier.

Radiochemists working in different international laboratories have developed several new extractants capable of a) partitioning of minor actinides from HLW as well as b) their mutual separation from trivalent lanthanides (which form a significant fraction of the fission products). The most promising extractants for a) are CMPO (Octyl-(phenyl)–N,N-diisobutyl carbamoyl methyl phosphine oxide), TRPO (Trialkyl phosphine oxide), DMDOHEMA (N,N'-dimethylN,N'-dioctylhexylethoxy malonamide) and TODGA (Tetraoctyl diglycolamide) and for b) are BTBP(2,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazine-3-yl)-2,2'-bipyridine) and DCPDTPA (Di-chlorophenyl-dithiophosphinic acids). Though each of these extractants have undergone extensive laboratory tests with simulated HLW solutions, only a few have been evaluated on pilot plant stage with genuine HLW. In recent years, there is growing interest in exploring the pyro-chemical methods in view of their distinct advantages like ability to process irradiated targets with short cooling periods and generation of low secondary waste.

Though the feasibility of transmutation of long lived radionuclides (present in HLW) into short lived radio nuclides using light water reactors (LWRs) was demonstrated in seventies, it is yet to be industrialised due to several technological as well as economical constraints. In the meantime, the concept of transmuting actinides and long lived fission products using dedicated sub-critical reactors had drawn the attention of nuclear physicists. This idea has gained further impetus in recent years due to the potential of using an accelerator-driven system (ADS) as an Energy Amplifier apart from transmuting long lived radionuclides present in HLW.

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SELECTIVE RECOVERY OF CESIUM USING HOLLOW FIBRE SUPPORTED LIQUID MEMBRANE CONTAINING CALIX[4]ARENE-BIS-2,3-NAPHTHO-CROWN-6

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Separation of radio-cesium from the HLW is important from the safe radioactive waste management point of view [1]. In addition, ^{137}Cs has applications as radiation source. Calix[4]arene-bis-crown-6 molecules in the 1,3-alternate conformation are reported to be extremely selective for Cs in the presence of large concentration of Na [2].

Solvent extraction methods involving calix[4]-bis-crowns have shown great promise for Cs recovery from alkaline as well as acidic waste solutions [3]. Recently, we have reported solvent extraction as well as supported liquid membrane (SLM) studies for selective recovery of Cs(I) from radioactive waste using calix[4]arene-bis-2,3-naphthocrown-6 (CNC) as the ligand using both nitrobenzene as well as 2-nitrophenyloctylether (NPOE) as the diluents [4]. From application point of view, hollow fiber supported liquid membranes (HFSLM) have a clear edge in view of their large surface area to volume ratio. The present paper highlights the much improved mass transfer rates and separation behaviour of ^{137}Cs obtained with CNC as the carrier in HFSLM.

Quantitative (>99.9%) Cs transport was possible in about 6 hours using 1x10^{-3} M CNC in 80% NPOE + 20% n-dodecane from a feed solution containing 3 M HNO3. Transport studies carried out as a function of feed acidity indicated peak transport rates at 3 M HNO3. Lower transport rates at lower acidity was ascribed to unfavourable DCs values on the basis of eqn. (1) and those at higher transport rates are ascribed to competitive co-transport of nitric acid.

$$\mathrm{Cs}^{+}_{(\mathrm{aq.})} + \mathrm{NO_3}^{-}_{(\mathrm{aq.})} + n\mathrm{L}_{(\mathrm{org.})} \rightleftharpoons (\mathrm{Cs.}n\mathrm{L})^{+}\cdot\mathrm{NO_3}^{-}_{(\mathrm{org.})} \qquad (1)$$

The membrane stability was excellent over a period of 120 hrs. Selectivity studies were also carried out by taking a mixture of radiotracers viz. ^{51}Cr, ^{59}Fe, ^{85,89}Sr, ^{137}Cs, ^{152,154}Eu and ^{241}Am, which represent some of the elements present in the high level waste, in the feed solution. The decontamination factor for all the metal ions was ~100. High decontamination factors as well as throughputs suggested possible application of the system for the recovery of radio-cesium from high level waste.

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PO-1-4-15 16078

APPLICATION OF ACETOHYDROXAMIC. FORMOHYDROXAMIC, AND ASCORBIA ACID IN NUCLEAR REPROCESSING: COMPLEXATION WITH TECHNETIUM00 AND IMPLICATIONS TO THE UREX PROCESS

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One of the final steps in the UREX+ reprocessing system is the separation of uranium from technetium. Currently, a technique under consideration is to use anion exchange resins to selectively remove pertechnetate from uranyl followed by competitive elution with ammonium hydroxide or nitric acid. We present the elution of pertechnetate from Reillex HP and Eichrom WBEC anion exchange resins with acetohydroxamic (AHA), formohydroxamic (FHA), and ascorbic acid (Asc); all form compounds with Tc while by-passing the production of ammonium nitrate which increases difficulty in Tc metal recovery for ultimate immobilization into a metallic waste form. Additionally, separation of Tc-AHA, Tc-FHA, and Tc-Asc from uranyl by extraction into tribultylphosphae (TBP) in dodecane is discussed with each compound. The properties of Tc-AHA, Tc-FHA, and Tc-Asc have been characterized by UV-Vis, EXAFS, Liquid Scintillation Counting (LSC) and various electrochemical techniques. The role and implication of Tc-AHA, Tc-FHA, and Tc-Asc in the UREX process and recovery of metallic Tc from each compound is discussed.

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THE RESULTS OF RADIOCHEMICAL MEASUREMENTS OF FUEL LEAK TEST AT UNIT 4 OF PAKS NUCLEAR POWER PLANT

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Background: Quite a high iodine activity was observed just after the restart of Unit 4 in 2008. The increase of iodine activity did not require Unit shutdown, and a decision was made to find the failed fuel assembly during the maintenance outage in 2009. A Höfer & Bechtel telescopic sipping device, which has been available in the power plant since autumn 2008, was used during the refuelling work at the end of the campaign, to identify the failed fuel assembly. Methods: With the help of the H&B apparatus, we carried out a complete sipping test of the entire Unit 4 reactor core of Campaign 22, in the course of the normal refuelling process. This method consists of the lifting of each fuel assembly, causing the external hydraulic pressure to decrease, as a result of which the damaged rods are expanded, and the accumulated radioactive material vented. This was the first time such device was used during refuelling straight after the shutdown of the reactor. The sipping device carries out on-line gas measurements and provides water samples for laboratory examination.

Results: During the test, each fuel assembly was raised by the Refuelling Machine, and the activity of the gas, which was recovered from the water pumped through the fuel assembly, was continuously measured with the use of a scintillation detector and the sample of water was laboratory analysed for composition. The water pumped through the fuel assembly was later analyzed with gamma-spectrometry method. The water in the refuelling pool was sampled every day for laboratory analysis and for tracing the test backgrounds. The variation, with the time, of the activity concentration of the caesium, iodine and xenon isotopes showed very similar tendencies during the sipping measurements. The highly soluble Xe gas showed high concentration at the beginning and reduced, within two days to the level of the other indicator isotopes (^{131}I, ^{134}Cs, ^{137}Cs). This high activity concentration also caused high background activity at the sipping detector. The activity values of ^{131}I and ^{137}Cs are normally used for the evaluation of water samples, because only the gamma line of ^{133}Xe corresponds with one of the gamma lines of ^{131}I, making the evaluation difficult. It may happen that, in fact, ^{131}I isotope is measured rather than ^{133}Xe. Since the activity of ^{131}I isotope was high, we had to have a complete spectral analysis carried out to allow the measurement of the actual activity of ^{133}Xe.

Conclusions: Both the on-line gas measurements and the water sample analysis indicated that the fuel assembly no. 70873 was failed. The on-line measurement results obtained showed a several order of magnitude increase in activity as compared to the background and thus positively identified the fuel assembly containing the defective rod. The water sample taken from fuel assembly 72554 showed some ^{133}Xe activity, which was significant when compared to the background level of the given time period. In this time period, the on-line gas measurement also exceeded the warning level, but did not reach the threshold of the emergency levels. For other nuclides measured in the water sample, no change was detected compared to the background. Thus, this fuel assembly can not be considered failed and can, therefore, be further used in the subsequent campaign.

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ROLE OF ENERGETIC TRITIUM CHEMISTRY ON DEVELOPING THERMONUCLEAR FUSION REACTORS

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Knowledge about chemical behavior of energetic hydrogen isotopes, especially tritium, in solid states has increasingly required for development of thermonuclear fusion reactors. In D-T fusion reactors, energetic tritium will be produced by the nuclear reactions of 6Li(n, 〈)T and 7Li(n, n’ 〈)T in lithium-breeding materials, and also will escaped from the D-T plasma, and then implanted into the plasma facing materials, such as graphite, beryllium, tungsten and so on. Both of them could behave hot-atomically in the lithium ceramics and plasma-facing materials, respectively. Especially, the chemical behavior of energetic tritium produced in the tritium breeding materials by the nuclear reaction is interested from the view point of radiochemistry. In the present paper, we will review hot atom chemical behavior of energetic tritium produced in the tritium breeding materials of fusion reactors.

Our previous experiments revealed that in thermal neutron-irradiated Li2O tritium existed in three chemical states of T+, T- and T0, whereas only T+ was existed in Li2O thermal-doped with tritium.[1] The present experiments also showed that T- species were eventually converted to the T+ species through the thermal annealing above 570 K for the ternary lithium oxide. These results showed that hot atom behavior made an important role to determine the recovery rate of hot tritium in the ternary lithium oxide in fusion reactor.

Recently, detail studies on kinetic of annihilation of irradiation defects induced by the nuclear reaction were carried out by means of Electron Spin Resonance (ESR)[2]. The measurements showed that there was a close correlation between the irradiation defects and tritium exiting states[3]. Moreover, extensive studies on kinetics of tritium release processes from neutron-irradiated lithium bearing materials by Thermal Desorption Spectroscopy (TDS) suggested that tritium migration triggered by the annihilation of the irradiation defects. From both of ESR and TDS results, we proposed a comprehensive migration model for energetic tritium produced in the ternary lithium oxide.

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PO-1-4-18 19459

IMPROVEMENT OF TECHNOLOGY FOR NITRIC-ACID EXTRACTION AFFINAGE OF URANIUM

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The process of extraction affinage of uranium at nuclear facilities results in generation of uranium-containing liquid waste -extraction raffinates -with concentration of nitric acid from 60 g/l up to 240 g/l. Before discharge into the tailing pit, the solutions are neutralized by calcium hydroxide (ammonium) that ensures formation of poorly soluble compounds of non-ferrous, heavy and radioactive metals. Thus, the saline nitrate -ion easily gets into the clay substratum and, migrating in it, affects the ecological balance in hygrographic network around the facility. So far, no acceptable methods with satisfactory technical and economic indices for denitration of liquid waste have been developed. For instance, removal of nitric acid from the liquid waste has not become widely used because of noticeable corrosion of structural materials due to the presence of the fluorine ion. To reduce consumption of nitric acid and discharge of nitrite ions together with liquid waste, we have developed the low-waste technology for nitric-acid extraction affinage of uranium, which presupposes use of urea nitrite as a recyclable salting-out agent. The said urea nitrate is obtained in the process of heat-free carbamide denitration of extraction raffinates. The distinctive feature of a suggested technology is that dissolution of uranium concentrate is carried out with a minimal excess of nitric acid using currently available process equipment at temperatures that are 10-15°C above routine working temperatures. Urea nitrate obtained in the process of carbamide denitration of extraction raffinates, is added prior to extraction to the solution of uranyl nitrate to ensure concentration of free nitric acid at 1.5-2.0 mol/l [1]. Extraction of uranium in the presence of urea nitrite proceeds without any complications. Filtrate obtained after removal of the urea nitrate sediment from extraction raffinate, undergoes galvanochemical treatment in the vertical vibration reactors in a field of “iron – carbon” galvanic couple with separation of uranium-containing iron hydroxides and subsequent selective carbonaceous leaching of uranium which is then returned to the initial stage of the process; this makes it possible to avoid irretrievable losses [2]. Liquid tailings purified by galvanochemical method are not ranked as liquid radwaste and do not need special storage conditions. To test the suggested technology, large-scale laboratory experiment has been performed at NCCP, Inc. It resulted in the production of ceramic uranium dioxide pellets through precipitation of ammonium polyuranate (ADU-process). The experiment has shown that the use of urea nitrate as a recyclable salting-out agent in the process of extraction affinage of uranium makes the total consumption of the nitric acid 1.5-2.0 times less, considerably reduces saline nitrite-ion discharge into the tailing pit, saves alkaline reagent used for neutrolization with complete maintaining of all the quality properties of the final product.

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PO-1-4-19 19467

REHABILITATION OF URANIUM PRODUCTIONS TECHNOGENIC WATERTANKS

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The stores of the liquid radioactive waste (LRW) are potentially dangerous, as in the course of their exploitation there is a radionucleads migration for the reservoir limits. It has been developed the technology of one conservation stage of the reservoir LRW – the purification of the pulpstore decantats at the general mineralization about 4 g/l and more which provides to decrease the uranium dimension (below 0.1 mg/l). For the decantats purification it has been used the galvanochemical method based on anode dissolution of the galvanic pair Fe-C iron by means of internal electrolysis which results the generation of iron hydrate polyforms in volume of a purified solution [1]. The effect of main galvanocoagulation process parametres (pH, contact time, solution expense, vibration frequency) on the purification efficiency has been investigated. It has been established, that the change of solution acidity and vibration frequency allows to regulate the deposit generation. The residual uranium concentration correlates with the content of a generated galvanoslime deposit. So at initial uranium concentration of 0.4-7.5 mg/l it is necessary to generate 0.5-1.6 g/l of galvanoslime deposit in the purified solution in order to provide the uranium permissible concentration. For the LRW purification it is possible to use vibrogalvanocoagulator of small productivity which will carry out a role of the supplier of a coagulant-sorbent. After dilution of the galvanoslime with initial decantat in 2-5 times residual concentration of uranium remains at level <0.1 mg/l. Produced galvanoslime is not only chemically stably, but also has the sorption properties to uranium of the initial decantat, that does possible to store galvanoslime under a mirror of the pulpstore or immobilizate it in the mintraloid matrixes. As a result of this research, it have been developed and offered some variants for purification of pulpstore decantats.

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PO-1-4-20 15424

DYNAMICS OF ENERGETIC HYDROGEN ISOTOPES IN CARBON-RELATED MATERIALS FOR FUSION REACTOR APPLICATION

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Graphite and carbon-related materials have a lot of advantages for usage of fusion structural materials because of its low induced activation and good thermal conductivity. Recently, the tungsten is also considered to have a potential for the usage of plasma facing materials due to low sputtering yield by energetic particles. Therefore, the combination usage of graphite-related materials and tungsten is thought for the design of fusion reactor.

One of the critical issues is that saturation of deuterium in graphite-related materials was high due to high affinity with hydrogen isotopes, more than 0.7 D/SiC, 0.4 D/C and so on. It is also known that the hydrogen isotope retention would be influenced by structure change of materials by high energy particle implantation. Therefore, knowledge of radiochemistry, especially hot atom chemistry is quite important to understand the hydrogen isotope recycling in carbon-related materials. This paper reviews the dynamics of energetic hydrogen isotopes in carbon-related materials, especially graphite, SiC and WC from the viewpoint of hot atom chemistry, and the trapping and detrapping mechanisms of hydrogen isotopes were summarized. The 3 keV deuterium ions (D_2^+) were implanted into the graphite, SiC and WC samples as a function of heating temperature and ion fluence. The chemical states of materials were evaluated by X-ray photoelectron spectroscopy (XPS). The deuterium retention was also estimated by Thermal Desorption Spectroscopy (TDS) using a quadruple mass spectrometer. It was found that D_2 TDS spectrum for graphite and SiC consisted of two desorption stages. However, the deuterium desorption temperatures for graphite were located at around 900 K and 1000 K, while those for SiC was 800 K and 1000 K, which corresponded to the desorption of deuterium bound to Si and C, respectively. For WC sample, it was desorbed in the temperature region from 300 to 700 K and at around 1000 K, indicating that most of deuterium was retained in the interstitial site of WC. The experimental results also indicated that the deuterium retention for higher temperature was reduced approximation one fifth of that for room temperature. In the presentation, trapping and detrapping mechanisms of energetic deuterium will be discussed.

SYNTHESIS AND CORROSION OF METALLIC TECHNETIUM IN ACIDIC MEDIA

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The isotope ^{99}Tc is problematic due to its high fission yield, long half-life, and complex solution chemistry. In the proposed UREX process, solution phase ^{99}Tc is separated from other elements, converted to the metal, and made into a suitable waste form. An appropriate waste form containing Tc metal should be convenient for disposal or transmutable into stable ^{100}Ru. However, little data on synthesis and the behavior of Tc metal in aqueous media exist. In order to better understand formation of the metal in solution, electrochemical synthesis has been performed. The resulting product was examined by a number of techniques with speciation determined by X-Ray absorption spectroscopy. Once characterized, a Tc metal electrode was constructed to study its corrosion mechanisms. . The electro-dissolution of Tc metal was examined in nitric and hydrochloride acid (0.1 M, 1 M, 2 M and 6 M) between 500 mV and 1300 mV/ Ag/AgCl. Corrosion rates and dissolution potentials were determined. The corrosion products were characterized by UV-Visible spectroscopy in solution and SEM and TEM on the electrode surface. Using the results previously obtained, the stability of Tc metal in acidic media is discussed and compared with other transition metals (Mo, Ru and Re). A corrosion mechanism for Tc metal is proposed.

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RECOMBINATION OF HYDROGEN AND OXYGEN IN FLUIDIZED BED REACTOR WITH DIFFERENT GAS DISTRIBUTORS

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The recombination of hydrogen and oxygen with molar ratio of 2:1 and flow rate of 2 Nm^3/h has been investigated in the fluidized bed reactor. It has been observed that the quick mixing of hydrogen and oxygen in the existence of Pt/Al2O3 catalyst is free of explosion and allows the effective recombination at the temperature of 373K. However, this highly exothermic reaction brings the much high temperature gradient in the fluidized bed. And the hot spot in reactor is sometimes higher than 1173K, causing the rapid deactivation of the catalyst and leading to the dangerous explosion. By adopting the multistage gas distributor, the concentration of hydrogen in the pristine gas distributed region (always in the bottom of the reactor) is effectively reduced and the temperature in the dense phase region of the catalyst can be controlled between 673 and 773K, allowing a stable and effective conversion rate of hydrogen up to 99.9997%. The present work provides a novel fluidization technology for the recombination of hydrogen and oxygen with high concentrations.

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CHLORINATION OF ANTIMONY AND ITS VOLATILIZATION TREATMENT FOR WASTE ANTIMONY-URANIUM COMPOSITE OXIDE CATALYST

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In 1960s, an antimony-uranium composite oxide catalyst (AUCOC) was created by a team who developed a famous acrylonitrile synthesis process, Sohio Process, in USA. The catalyst was in a form of that the composite oxide of antimony and uranium was supported on porous silica beads. The contents of antimony and uranium in the catalyst were approximately 30 and 15%, in mass respectively. Several Japanese chemical companies employed AUCOC to synthesis acrylonitirile until the early 1970s. Then, they changed the catalyst to more hazardless one, such as a molybdenum -bismuth-iron composite oxide, etc., and they stored AUCOC waste without any treatment. In Japan today, 200 tons as metallic uranium estimated as AUCOC waste stored in the several companies with the rigid managements under Japanese legislation.

In order to remove uranium from AUCOC waste, we considered the application of the uranium extraction with supercritical carbon dioxide and tri-*n*-butylphosphate (TBP)-nitric acid complex, which is known to be effective to extract uranium from uranium oxides. The supercritical carbon dioxide has appropriate solvent properties for the extraction, *i.e.*, its high diffusivity enables the extraction of uranium contained in small pores, and it becomes gas by depressurization resulting in the reduction of secondary waste treatment compared with the conventional acid leaching. For applying this method, there is a requirement that the target uranium compounds should be dissolved in nitric acid, *e.g.*, uranium dioxide is dissolved in nitric acid as well as in supercritical carbon dioxide with TBP-nitric acid complex. Prior to the extraction, AUCOC was tried to dissolve in nitric acid, however, it did not dissolved. Uranium oxide seemed to be undissolve by forming a composite oxide with antimony oxide. If antimony is separated from AUCOC destroying the composite oxide, the supercritical fluid extraction method becomes applicable to the removal.

In the present study, as pretreatment for the supercritical fluid extraction, we proposed the chlorination and volatilization treatment for AUCOC. It is known that antimony (III) chloride has relatively low boiling point at 497 K. We chose hydrogen chloride gas as a chlorination reactant. A quartz boat containing 50 mg of AUCOC was placed in a quartz tub reactor set in a furnace heated at 1073 K. Hydrogen chloride gas was fed to the reactor and contacted with the catalyst for 3 hr. After the treatment, 21% of weight loss and color change was confirmed. By an X-ray diffraction analysis, the peaks of the composite oxide of antimony and uranium disappeared with the treatment while those of uranium oxide appeared. It was found that the chlorination and volatilization treatment was effective to separate antimony from the composite oxide of antimony and uranium, leading to the next step of the supercritical fluid extraction of uranium.

PO-1-4-24 16066

A STUDY OF 2.6-BIS[(BIS(2-N-OCTYL)PHOSPHINO)METHYL]PYRIDINE N,P,P`-TRIOXIDE IN SOLVENT EXTRACTION OF ACTINIDES

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Organophosphorus solvent extraction reagents have played a particularly important role in actinide extraction. A wide variety of compounds of varying basicity and geometric arrangement of donor groups have been reported. These ligands are important from a fundamental perspective, but also technologically. In this report, the ability of the trifunctional organophosphorus ligand 2.6-bis[(bis(2-n-octyl)phosphino)methyl]pyridine N,P,P`-trioxide (TO(NOPOPO) to extract Eu(III), Am(III), Th(IV), Pu(IV), Np(V), and U(VI) from acidic media has been tested. The relative extraction efficiency of actinide ions (Th(IV), Pu(IV) , Am(III) , Np(V) and U(VI)) by TO(NOPOPO) changes in a more-or-less predictable manner with the oxidation state of the cation. The stoichiometry of the phase transfer reaction of the actinides into TO(NOPOPO)/toluene has been established and selected thermodynamic parameters determined.

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DISSOLUTION AND EXTRACTION OF URANIUM DIOXIDE USING IONIC LIQUID AND SUPERCRITICAL FLUID CARBON DIOXIDE

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Supercritical fluid carbon dioxide (sc-CO_2) and ionic liquids (IL) are considered green solvents for chemical reactions and separations. Research in sc-CO_2 dissolution and extraction of lanthanides and actinides started in the early 1990s. Direct dissolution and extraction of uranium dioxide and lanthanide oxides in sc-CO_2 can be achieved using a CO_2-soluble tri-n-butylphosphate-nitric acid complex of the form $TBP(HNO_3)x(H_2O)y$. The extracted uranium species in sc-CO_2 is $UO_2(NO_3)_2(TBP)_2$. Current industrial demonstration by Areva NP for recovering enriched uranium from the ash waste produced by the light water reactor fuel fabrication process using a sc-CO_2 process is presented.

Direct dissolution of uranium dioxide and lanthanide oxides in an IL [bmin][Tf_2N] (1-alkyl-3-methylimidazolium cation and bis(trifluoromethylsulfonyl)imide anion) using $TBP(HNO_3)_{1.8}(H_2O)_{0.6}$ under ambient temperature and pressure has also been demonstrated recently. No aqueous phase is formed in the IL dissolution process. The uranium and lanthanide species dissolved in the IL phase can be effectively transferred to sc-CO_2 and the IL can be recycled for repeated use. This IL-sc-CO_2 hyphenated dissolution/extraction method suggests another green technique for recycling enriched uranium from nuclear wastes. Potential applications of these emerging green techniques for nuclear waste management are discussed.

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DEVELOPMENT OF POROUS URANIUM CARBIDE FOR THE SPEX PROJECT

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Isotope Separation on-line facilities are gaining significant interest worldwide because of their importance in the study of heavy elements formation and the processes that govern the universe. The SPES project[1], now under development at LNL-INFN will make use of a 40 MeV proton beam directly impinging on seven uranium carbide separate thin discs. The main obstacle for the success of such facilities is the capability of extracting the produced isotopes, the selective ionization of the extracted isotopes and their transportation to the experimental areas. The process of isotopes extraction is governed by diffusion and effusion laws. For this reason, the ideal material for high yield target should be capable of working at temperature as high as 2000 °C, possess small grain size, high porosity percentage and a high interconnectivity degree. The standard route for the production of uranium carbide for ISOL facilities consists on the direct carbothermal reaction of uranium oxide and a proper source of carbon in excess (traditionally graphite) following reaction (1):

$$UO_2+6C \longrightarrow UC_2+2C+2CO \qquad (1)$$

By this route tetragonal uranium carbide dispersed in graphite (UC2/C equal to ½) is produced. The material bulk density ranges from 3 to 4 g/cm^3 and the porosity is the direct consequence of CO release. Within the SPES Project much effort is given to the development of novel uranium carbide targets possessing tailored properties[2,3]. The use of different uranium precursors, source of carbon and pores formers will be presented and their effect on material properties and release efficiencies will be analyzed.

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ABSORPTION SPECTRA AND CYCLIC VOLTAMMOGRAMS OF URANIUM SPECIES IN MOLTEN LITHIUM MOLYBDATE–SODIUM MOLYBDATE EUTECTIC AT 550 °C

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The study of a pyrochemical process by using an alkaline molybdate melt has been carried out as a candidate reprocessing process for spent nuclear oxide fuels. This alkaline molybdate melt has a useful characteristic, which is an ability to dissolve uranium oxides, such as UO_2 in a short time. In the previous study [1], the UO_2 pellet was dissolved into molten sodium molybdate mixtures of Na_2MoO_4–Na_2MoO_7 at 750 °C and uranium species dissolved in the melts were recovered as UO_2 particles by electrolysis at 700 °C. However, the coordination circumstances of uranium species in alkaline molybdate melts have not been studied. Since the melting point of Na_2MoO_4 is high and since it also reacts with the spectrum measurement cell made of quartz, the absorption spectrum has not been ever reported.

In this study, absorption spectra of uranium species dissolved in molten lithium molybdate–sodium molybdate eutectic of $0.5Li_2MoO_4$–$0.5Na_2MoO_4$ mixture at 550 °C were measured by UV/Vis/NIR spectrophotometry, and their redox reactions were also investigated by cyclic voltammetry. The melting point of Li_2MoO_4–Na_2MoO_4 eutectic is lower than that of Na_2MoO_4 or Na_2MoO_4–Na_2MoO_7 mxtures [2], and the corrosion damage of the quartz cell can be avoided. As the results of spectrophotometry, it was found that the major ions of uranium species dissolved in the melt were uranyl pentavalent ions of UO_2^+, whose observed absorption spectra were similar to those of UO_2^+ in molten chlorides [3]. After purging dry oxygen gas into the melt, the absorption peaks of UO_2^+ decreased and UO_2^+ was thought to be oxidized to the uranyl hexavalent ions of UO_2^{2+}. In the cyclic voltammetry, two platinum wires 1 mm in diameter were used as the working and counter electrodes.

The reference electrode utilized was composed of a PYREX tube with about 0.5 g of Li_2MoO_4–Na_2MoO_4 eutectic and a platinum wire. When the uranium species were not contained in the melt, it was confirmed that alkali metals were deposited on the working electrode at –0.7 V (*vs.* reference electrode) and the lithium molybdenum oxide compounds of Li_2MoO_3 and $Li_6Mo_2O_7$ were deposited on the counter electrode at 1.0 V. In addition, a small reductive reaction was observed at –0.3 V. When UO_2 was dissolved into the melt, the reductive reaction of the uranium species was observed at –0.2 V.

This suggests that the uranium species dissolved in the melts could be recovered as mixed uraniummolybdenum oxides by electrolysis, since the reduction potential of uranium species is close to the deposition potential of the molybdenum oxide compounds.

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STUDY OF ACTINIDE AND LANTHANIDE COMPLEXATION BY ORGANICALLY MODIFIED MESOPOROUS SILICA

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Inexpensive high surface area mesoporous materials are functionalized with organic molecules to create lanthanide- and actinide-specific binding sites. These materials have a wide range of expected applications in environmental sequestration, separations for nuclear waste reprocessing, or element-specific sensors. Potentially actinide-specific trialkoxysilane ligands are synthesized, then grafted into a monolayer inside the pores of mesoporous silica (SBA-15, ~10 nm pore diameter). Materials are characterized with solid-state nuclear magnetic resonance spectroscopy (NMR), gravimetric analysis, and infrared spectroscopy. The important features of these ligands, such as the functional groups and chelating ring size will be optimized toward selective actinide complexation by systematic variation informed by quantum computational modeling. Binding affinity of the functionalized material is determined by batch complexation studies as a function of pH, measured using inductively coupled plasma-mass spectrometry (ICP-MS). Eu(III), Ce(III), and Zr(IV) are used as initial test species before examining radioactive actinide elements and focusing on specific oxidations states. Functionalized materials are tested for binding affinity toward Pu(VI) using liquid scintillation counting (LSC). The systems that seem most promising in initial tests will be further explored with respect to solution pH, target species concentration, binding kinetics, and the presence of competing ions using ICP-MS and LSC.

EVALUATION OF COVALENT INTERACTIONS IN ACTINIDE COORDINATION COMPOUNDS

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Complexing agents containing soft–base (e.g., N or S) donors such as dithiophosphinic acids have significant potential for the efficient separation of trivalent actinides, An(III), from lanthanides, Ln(III). A family of dithiophosphinic acids (DPAH) developed at the INL has shown unprecedented selectivity for americium and curium over lanthanides in acidic solution. As the actinide series is crossed from U to Cm, the extent covalency observed in the metal ligand bond is expected to decrease due to the decrease in the spatial extent of the 5f orbitals. UV-vis, infrared, and Raman spectroscopies are used to quantify the extent of covalency in the An(III)-DPAH coordination compounds. By systematically studying variations in An(III)-DPAH coordination complexes, we plan to develop a detailed understanding of the interactions of Ln(III) and An(III) ions with soft donor ligand systems. This detailed understanding holds the promise of providing great insight into the nature of actinide interactions with soft-donor bases.

THERMODYNAMICS OF Th(IV) COMPLEXATION WITH DICARBOXYLATE LIGANDS : A POTENTIOMETRIC AND CALORIMETRIC STUDY

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The migration of actinides is greatly influenced by various organic and inorganic complexants present in the aquatic environment. In order to predict their migration behavior, it is important to understand their interaction with these complexants. Complexation of actinides by natural organic matter, viz., humic acid and fulvic acid as well as their degradation products in the form of small organic acids has, therefore, been a subject of considerable interest during the last few decades. In the present study the thermodynamics of complexation of Th(IV) (analogue of tetravalent actinides) with dicarboxylates, namely Malonate, Succinate, Glutarate and Adipate has been studied using potentiometric and calorimetric technique. In addition to being the model compounds of humic acid these carboxylates are also present in the natural environment. The thermodynamic parameters (e.g., ΔH) are not only essential from fundamental point of view but are also required to estimate the stability constants at elevated temperatures (viz near the geo-repositories) using Van't Hoff equation. In addition to enlarge the thermodynamic database, the work presents a systematic study to understand the effect of carbon chain length (n) ($^{-}OOC-(CH_2)_n-COO^{-}$) of dicarboxylates on the thermodynamics of their complexation with Th(IV). The stability constants were determined using potentiometry and logK obtained were used to analyze the calorimetric data to obtain ΔH and ΔS of complexation. ΔH for all the dicarboxylate complexes are positive and large entropy associated with the complexation make the free energy negative, indicating that the complexation reactions are entropy driven. This behaviour is characteristic of reactions involving hard acid metals and hard base ligands. The higher TΔS of dicarboxylates compared to known values for monocarboxylates suggest the chelate formation through two carboxylate groups. The stability constant decreases as the number carbon atoms (n) in dicarboxylates increases from malonate (n=1) to glutarate (n=3). However on further increasing n from glutarate (n=3) to adipate (n=4) the stability constant decreases. The TΔS was nearly constant for all the dicarboxylates and the variation in ΔG was mainly governed by change in ΔH. Nearly constant TΔS values for all dicarboxylates suggest that the extent of dehydration is similar in all the complexes and increase in volume of ligand does not affect the dehydration of metal ion significantly. The ΔH increased from malonate (n=1) to glutarate (n=3) and again decreased in adipate (n=4). This observation could be explained in terms of the effect of ring size stability in the complex formed and the basicity of the ligand on ΔH. The opposing effect of the two factors might be responsible for the minimum in ΔH at glutarate

ADSORPTION BEHAVIORS OF F-ELEMENTS ON TERTIARY PYRIDINE AND QUATERNARY PYRIDINIUM RESINS

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We have been studied the separation of trivalent actinides and lanthanides by chromatographic techniques using tertiary pyridine resin. The group separation was achieved by using tertiary pyridine resin in HCl / methanol mixed solution [1]. The mutual separation of actinides [2,3] or lanthanides [4] was achieved by using HNO_3 / methanol mixed solution. The adsorption behaviors of actinides and lanthanides on tertiary pyridine resin in HCl system and HNO_3 system are confirmed to be different from each other; namely, actinide are strongly adsorbed compared to lanthanides in HCl system, while in HNO_3 system, the adsorption strength is depend on not actinides or lanthanides but ionic radii. The tertiary pyridine resin has two functions, one is a function of weakly basic anion exchanger, and another is a function of soft donor ligand. We speculate that the soft donor function of pyridine group is appeared in HCl system, and anion exchange function is appeared in HNO_3 system in the case of f-elements adsorption on pyridine resin. The quaternary pyridinum resin was manufactured by quaternizing pyridine group of tertiary pyridine resin. The quaternary pyridinium resin has only one function of strongly basic anion exchanger. The adsorption experiments of trivalent actinides and lanthanides on quaternary pyridinium resin were carried out in HCl system and HNO_3 system. The adsorption mechanism was discussed by comparing the tertiary pyridine resin and quaternary pyridinium resin. It was confirmed that the trivalent actinides and lanthanides can be separated by quaternary pyridinium resin in HCl and the adsorption behavior on quaternary pyridine resin in HNO_3 system is similar to tertiary pyridine resin. From these results, it was concluded that the f-elements adsorb on the resin by mechanism of ion exchange in HNO_3 system and on the other hand in HCl system, the adsorption mechanism is attributable to coordinate bonds of pyridine and f-elements.

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ELECTROCHEMICAL STUDIES ON MICROBIAL U(VI) REDUCTION

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The bioreduction of U(VI) is an important phenomenon affecting uranium migration in anaerobic environments. In the bioreduction by Shewanella species, ctype cytochromes have been thought to catalyze the reduction at the cell surface. On the other hand, it has been recently suggested that flavins secreted by Shewanella species act as extracellular electron shuttles. In the present study, we investigated the surface catalytic reduction of U(VI) on Shewanella putrefaciens and the FMN mediated extracellular reduction of U(VI) by electrochemical methods. To examine the catalytic reduction on the cell surface, a membrane electrode containing S. putrefaciens cells were constructed. A small amount of the cell suspension was deposited onto the Au working electrode and covered with a piece of dialysis membrane. A Pt wire and an Ag/AgCl wire were used as a counter electrode and a reference electrode, respectively. The cyclic voltammograms (CVs) were obtained at various U(VI) concentrations in the buffer solution of 20 mM sodium citrate and 10 mM HEPES of pH 6.4. In the absence of U(VI), no reduction peak was detected in the potential rang of 0.7 to 0 V. In the presence of U(VI), a reduction peak was observed at 0.6 V and it increased with U(VI) concentration. The reduction peak was scarcely observed using the membrane electrode without the cells. These results indicate that the cell surfaces provide the site for catalytic reduction of U(VI). The CVs of FMN were obtained by a normal Au electrode at various U(VI) concentrations in the buffer solution of pH 6.0. In the absence of U(VI), a couple of redox peaks was observed at 0.36 V. In the presence of U(VI), the reduction peak increased and the oxidation peak decreased with a rise in U(VI) concentration. These results indicate that FMN mediates the reduction of U(VI). In this study, we electrochemically confirmed the both reduction mechanisms of U(VI), the direct catalytic reduction on the cell surfaces and the FMN mediated reduction.

PO-1-7-7 19880

SOLVENT EXTRACTION OF TRIVALENT ACTINIDES WITH DI(2-ETHYLHEXYL) PHOSPHORIC ACID AND THENOYLTRIFLUOROACETONE

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Chemical properties of trivalent actinides heavier than Am as well as the trivalent lanthanides depend largely on their ionic radius. However, extraction behavior of the trivalent actinides such as Am and Cm was reported to be different from that of the lanthanides which cannot be explained only in terms of the radii [1]. It is, therefore, interesting to study chemical properties of Am^{3+} through Lr^{3+} with comparing with those of the lanthanides. In particular, few chemical studies of the heaviest actinides with atomic numbers Z ≥ 101 [2] were so far conducted because of low production rates in heavy-ion induced nuclear reactions and their short half-lives. In this work, the extraction behavior of the trivalent actinides into di(2-ethylhexyl)phosphoric acid (HDEHP) and 2-thenoyltrifluoroacetone (HTTA) was studied together with trivalent lanthanides.

The extraction of Am, Cm, Cf, and lanthanides (excluding Pm) from 0.01 – 5 M nitric acid into 0.01 – 1 M HDEHP in benzene was performed. Equal volume of each phase was mixed in a polypropylene tube and was then shaken in an incubator (31 ± 1 °C) for 20 min. After centrifugation and phase separation, the pH value of the equilibrated aqueous phase was measured. The distribution ratios of nonradioactive lanthanide isotopes were determined using ICP-MS by measuring the concentrations of metals in the aqueous phase and in the organic phase (back extracted to aqueous solution), while those of the radioactive actinide and lanthanide isotopes were obtained by γ-ray spectrometry with Ge detectors and α-particle spectrometry with Si PIN diodes detectors. Extraction constants of those elements were determined by a fit of the extraction reactions to the variation of the distribution ratios.

The extraction constants of the lanthanides become larger as an increase of a reciprocal square of the ionic radius corresponding to charge density (Fig. 1). Comparing Cf with Eu having similar ionic radii, the extraction constant of Cf is larger than that of Eu. On the other hand, comparing Am with Nd, the extraction constant of Am is smaller than that of Nd. This tendency is qualitatively consistent with the earlier report [1]. We will further investigate the extractiothe tendency in the heavier actinide region. The extraction of Am, Cm, Cf, Fm and Md into HTTA in carbon tetrachloride from mixed solution of hydrochloric acid and ammonium chloride (pH 2.7 – 3.5) was also performed together with lanthanides (Y, Ce, Pm, Eu~~,~~). The isotope ^{255}Md ($T_{1/2}$ = 27 min) was produced in the ^{248}Cm(^{11}B,4n) reaction using the AVF cyclotron at RIKEN and ^{250}Fm ($T_{1/2}$ = 30 min) was produced in the ^{238}U(^{16}O,4n) reactions using the AVF cyclotron at RCNP, Osaka University. The result showed that extraction constants of the actinides are larger than those of lanthanides with similar ionic radii.

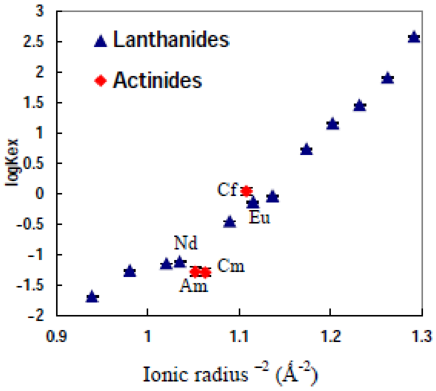

Fig.1 Extraction constants of lanthanides, Am, Cm, and Cf with HDEHP.

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EXAFS ANALYSES OF URANIUM(IV) AND THORIUM(IV) COMPLEXES IN $CaCl_2·6H_2O$ HYDRATE MELT

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The molten hydrated salt, which is generally called hydrate melt, is a very highly concentrated electrolyte. Because of the limited amount of water, the hydrate melt gives a characteristic chemical behavior to solutes. Dependence of the activity coefficient of ions on the water content shows a different trend compared to that in the water-abundant solutions. In order to clarify the characteristic variation of the activity coefficient of ions of f-elements in hydrate melts, some spectroscopic analyses, they are, electronic absorption spectrometry, fluorescence spectrometry, emission lifetime analysis, Raman spectrometry, and extended X-ray absorption fine structure, EXAFS analysis, have been performed [1]. According to our EXAFS measurements for UO_2^{2+} in calcium chloride hydrate, $CaCl_2·nH_2O$, the coordination number of Cl^- ions in the coordination sphere of UO_2^{2+} decreased from 2.2 to 1.8 with the increase of water content from $CaCl_2·6H_2O$ to $CaCl_2·10H_2O$, while the hydration number in it increased from 1.4 to 2.1 [2].

In the present study, we studied the coordination spheres of the U^{4+} and Th^{4+} in $CaCl_2·nH_2O$ hydrate melts by EXAFS measurement. For U^{4+} species, three peaks were observed at $\Delta + R = 1.3$, 1.9, and 2.2 Å in Fourier transforms. The second and third far peaks were assigned to be the coordinations of U–O and the coordination of U–Cl, respectively. From the results, the coordination numbers of Cl– and H_2O of U^{4+} species in $CaCl_2·6H_2O$ were close to those in 14 M LiCl melt, in which the concentrations of Cl^- of both media was almost the same. Hennig et al. [3] found that the combined coordination number of Cl^- and H_2O of the U^{4+} species was 9 at low concentration of Cl^- while a smaller coordination number of 8 for 9 M LiCl. We also measured the EXAFS for Th^{4+} complexes and discuss the difference in the coordination circumstance of Th^{4+} complexes between these media.

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PO-1-7-9 12422

THE MOLECULAR STRUCTURE AND POTENTIAL ENERGY FUNCTION OF Li-M (M=Be, Pb, Bi, Th, U) DIATOMIC MOLECULE

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Using hybrid density functional theory (B3LYP) method, in conjunction with the relativistic effective core potential SDD for M (M = Pb, Bi, Th and U) atoms and all-electron basis set AUG-cc-pVTZ for Li and Be atoms, the molecular structures of LiM (M = Be, Pb, Bi, Th and U) were optimized. The potential energy functions of the corresponding molecules were studied. The spectral data, force constant, charge population and dissociation energy data of LiM (M = Be, Pb, Bi, Th and U) molecule were obtained. The results show that the bond lengths and harmonic vibration frequencies of the ground state LiM (M = Be, Pb, Bi) molecules are in agreement with the available experiments. The ground-state structures of LiTh and LiU molecules were obtained for the first time after different spin multiplicities tested. The spin multiplicity of 4 of the ground-state LiPb molecule was first predicted. In all studied ground-state molecules, the charge transformation from Li to M atoms were found by natural bonding orbital analysis (NBO). Wiberg bond indices and the calculated dissociation energies show that the ground state LiPb molecule are more stable than that in the excited state, while the ground state LiTh and LiU molecules are less stable than the corresponding molecules in the excited state, respectively.

PO-1-7-10 20682

MEASUREMENTS OF MOBILITY FOR ACTINIDES AND LANTHANIDES USING CAPILLARY ELECTROPHORESIS, AND ITS APPLICATION TO SHORT-LIVED NUCLIDES

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It is recognized that trivalent lanthanides and actinides show similar chemical and physical properties. However, information on the chemical properties of the heavy actinides is still limited because several heavy actinides are short-lived and the production of these actinides requires an accelerator. In this study, we derived the information on the chemical properties from the capillary electrophoretic mobility. Moreover, we measured the capillary electrophoretic mobility of the short-lived nuclides of lanthanides produced by an accelerator to apply to short-lived heavy actinides in the future.

The lanthanide multitracer was produced by nuclear spallation reaction of ^{197}Au(14N,X) at the E3b course of the RIKEN Ring Cyclotron, and was obtained by separation from the target material and other radioactive elements. Am(III), Cm(III), and Cf(III) tracers were added to the multitracer solution. This sample solution was injected into a capillary, followed by the electrolyte solution containing HIBA/acetic acid. The measurements of mobility for the trivalent lanthanides and actinides were performed under a voltage of +30 kV. The sample eluted from the capillary end was fractionalized. The radioactivity of each fraction was measured by alpha- and/or gamma-ray spectroscopy. In the accelerator experiments, the short-lived lanthanides were produced by Ln(^{16}O, xn) reaction and transported with the KCl aerosol/He gas to the laboratory. The aerosol was dissolved in an aqueous solution, and then the mobility was measured by capillary electrophoresis.

Figure 1 shows the plots of electrophoretic mobility against inverse of ionic radius of trivalent metal ion with the coordination number 8 (CN 8). In trivalent lanthanides and actinides, the mobility in this experimental condition decreased with decreasing ionic radius. The mobility of metal ions is in the order of ionic radius more than CN 8. From the correlation between the mobility and ionic radius, the ionic radius of Cm(III) with CN 8 was calculated. The stability constants of Am and Cm with 2-hydroxyisobutyrate and/or acetate were also calculated using the correlation between mobility and each of the stability constants of lanthanides.[1] The short-lived nuclides of lanthanides using the accelerator was successfully separated and their behavior is similar to those of the off-line experiments. This method is applicable to measure mobility of short-lived heavy actinides produced using the accelerator. The present study includes the results of the efficient separation and analysis of nuclear fission products for reprocessing systems entrusted to Osaka University by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

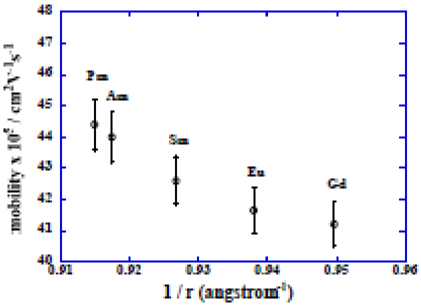

Figure 1. The plots of electrophoretic mobility against the inverse of ionic radius (CN 8).

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PO-1-8-1 19984

RAPID ENVIRONMENTAL ANALYSIS USING MOLTEN SALT FUSION SAMPLE PREPARATION

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The need for rapid methods for isotopic identification of environment samples, including transuranic materials, is very important. Now with an increase in processing, production, transport, and the danger they present to the environment; real time rapid methods of analysis are essential. Unique circumstances require a rapid method capable of separation and identification of select nuclear isotopes. The method needs to be robust enough to accommodate a fused silicon matrices, yet simple enough to be performed in the field under not so ideal conditions. Depending on matrix characteristics the sample may have to be completely dissolved before isotopic identification is possible. The main underlying assumption of this work is the sample to be analyzed may be silicate in form. This process assumes that metals in the sample have been incorporated into the matrix structure preventing easy digestion. Surface contamination may be insufficient to warrant direct leaching.

The main objective is solid dissolution into an aqueous liquid to produce a homogenous mixture so that subsequent separations and isolations can be performed to identify a specific isotope. This process uses changes in oxidation, chemical exchange, decomposition, or rearrangements to form constituents that are more soluble in aqueous solution. We used a molten-salt fusion, dissolution in dilute nitric or hydrochloric acids, with subsequent separation using ion exchange, direct deposition, and counting by αγ-spectrometry. This method is ideal for silicate samples containing a high percentage of sand or liquid samples. The preparation is robust enough so it can handle large amounts of metals i.e. such as iron. The process has been tested using alpha and gamma spectroscopy with reasonable results and a turnaround time of 4 hours depending on count time required. Minimum Detectable Amounts of 1 dpm α and 14 dpm γ on select emitters can be obtained with a count time of approximately one hour.

The success of any analytical procedure is determined by the completeness of the sample preparation including sample dissolution, separation, and isolation of the isotopes of interest. The reliability of a given method depends on the qualitative and quantitative conversion of a sample into a homogenous solution. In this instance homogenous refers to the complete dissolution and availability of the material of interest. Historically sample preparation was the bottleneck in sample analyses affecting turnaround and throughput. Advances in instrumentation and the improvements in detection methods facilitate the movement to smaller samples size, allowing for a simplification of the sample digestion process.

PO-1-8-2 15760

THE LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITE OF RUNIT DOME ON ENEWETAK ATOLL, MARSHALL ISLANDS: ITS HISTORY, CONSTRUCTION, AND NEED FOR CHARACTERIZATION AND MONITORING

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Following cessation of atmospheric testing of atomic weapons in 1963, the Pacific Proving Grounds of the United States (U.S.) located at Enewetak Atoll remained under the jurisdiction of the U.S. Department of Defense. It was not until the early 1970s after extensive characterization of fallout disposition in and around the atoll, that consideration was given to cleanup and return of the atoll to the people of Enewetak. The U.S. Army Corps of Engineers conducted a limited cleanup program on Enewetak Atoll between 1977 and 1980 under a structured agreement between various U.S. agencies. Cleanup entailed removal of top soil from several atoll islands and moving it to the most contaminated island of Runit. The contaminated material was subsequently mixed 10-15% by weight with Portland cement and clay and entombed (tremied below water line and bulldozed above) inside of an unlined test crater approximately 120 m in diameter. The filled material was covered with a 45 cm thick concrete dome cap to construct an apparent environmental seal. The site to now known as the Runit Dome.

Radionuclide inventories beneath Runit Dome were assessed at the time of the cleanup effort, and later revised, and shown to comprise approximately 15 Curies of transuranic waste. No records of fission product inventories beneath Runit Dome were ever developed. The U.S. Department of Energy has since developed a comprehensive individual radiological protection monitoring program at Enewetak and has historically conducted periodic environmental monitoring studies around the atoll. The general consensus from these environmental studies and predictive dose assessments is that Runit Dome does not pose a significant excess radiological risk to the people living on Enewetak Atoll. This is clearly supported by the results of the individual monitoring programs based on whole body counting and plutonium bioassay. However, Runit Dome does constitute a Low-Level Radioactive Waste Disposal Site and, at least within the U.S., would fall under more stringent requirements for site management and routine monitoring. Moreover, open communication of the buried waste with intruding ocean water and local groundwater was previously concluded based on water elevations observed in exploratory holes drilled not long after the dome was constructed.. Also, an ammonia and rotten egg smell emitted from these wells further indicating strong anoxic conditions developed due to decaying organic matter, illustrating the potential for redox-mediated aqueous transport of actinides. Environmental risk assessments performed on Runit Dome entailed only a catastrophic release scenario that projected that if the radionuclide inventory were spread throughout the atoll lagoon it would be dwarfed by the existing radiologic load presently adsorbed to bottom sediments. A more probable release scenario, characterized by localized leaching and migration into the immediate surroundings, would likely be facilitated by dissolution/complexation reactions with mineral and organic matter under low-pH anoxic conditions, followed by concentrated re-deposition in oxidized zones and/or uptake by plant roots. This is most relevant to plutonium transport. The likely high dissolved organic matter content of anoxic groundwater beneath the dome can form mobile complexes with low oxidation state Pu species, followed by re-concentration on Fe-oxide developed downgradient at oxidation boundaries near the waste boundaries. Consequently, this risk scenario justifies the need to develop a groundwater monitoring plan before any potential high radiation spreads beyond the site boundary. This monitoring coupled to predictive tools would further improve public awareness of the minimal risk posed by Runit Dome and alleviate any lingering doubts to its safety.

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ASPECTS OF RADIONUCLIDE CHEMISTRY IN THE NEAR-FIELD OF A CEMENT - BASED ILW DISPOSAL CONCEPT IN THE UK

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The Nuclear Decommissioning Authority (NDA) has been given responsibility for planning and implementing geological disposal in the UK and has set up the Radioactive Waste Management Directorate (RWMD) to develop an effective delivery organisation to implement a safe, sustainable and publicly acceptable geological disposal programme. One of the main programme objectives of RWMD is currently to develop a generic Disposal System Safety Case to assess the safety and environmental implications of a Geological Disposal Facility (GDF) for radioactive wastes for a range of generic geologies. One of the illustrative disposal concepts considered by NDA-RWMD for the disposal of Intermediate-Level Wastes and some Low-Level Wastes is that of grouted waste packages surrounded by a cementitious backfill. As part of a multi-barrier approach to retarding the migration of radionuclides, the backfill will be required to maintain a high pH environment designed to act as a chemical barrier to the movement of key radionuclides such as actinides which are least soluble in their lowest oxidation states and in the form of (hydr)oxides). The backfill, in addition to the waste encapsulation grouts and the presence of iron corrosion products will also reduce the mobility of some radionuclides by presenting surfaces on which they may sorb and, therefore, be removed from the porewater. However, UK Intermediate Level Waste contains a significant amount of solid organic polymers such as halogenated and non-halogenated plastics, rubbers, ion-exchange resins and cellulosic materials. Much smaller quantities of complexing agents may also be present. These, and some degradation products of the solid polymers, may form water soluble, and therefore mobile, complexes with key radionuclides. A process based understanding of the role of these potential complexants is therefore essential to support a safety case. Recently, we have undertaken a number of projects concerned with developing a better understanding of the role of these complexing agents and the results from these studies will be presented. One of the projects is concerned with cellulose and its degradation products, primarily α-isosaccharinic acid (ISA), and their effect on the solubilities of nickel, cadmium and thorium in solutions of sodium or calcium isosaccharinate, cellulose degradation product mixtures (CDP) and NRVB equilibrated water (water equilibrated with Nirex Reference Vault Backfill material). LC-MS, NMR, IR and UV analysis were used to analyse the degradation products and HPLC, with radiometric detection, and C-13 and solid state NMR were used to give information on the nature of the complexes. Results have indicated that components of CDP other than ISA have the ability to affect radionuclide solubility. Another project is concerned with the effect of "as-disposed" of complexants such as EDTA, DTPA, citrate and oxalate on the solubilities of radionuclides and these results will also be presented. Finally, longer–term experiments are underway to demonstrate long-term chemical containment in the near-field and these experiments will be described.

DISTRIBUTION COEFFICIENT OF 7Be IN OVERLAND FLOW ALONG A FORESTED HILLSLOPE: FIELD MEASUREMENTS AND LABORATORY BATCH EXPERIMENTS

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Beryllium-7 is a naturally occurring radionuclide that reaches land surface mostly through wet fallout. After deposition, ^{7}Be is retained in the uppermost soil layers. Beryllium-7 has been used as a unique tracer in numerous studies on geomorphologic and fluvial transport processes as have other fallout radionuclides, especially anthropogenic ^{137}Cs and lithogenic ^{210}Pb. Adsorption behavior, especially the distribution coefficient during input by precipitation and runoff as overland flow, must be understood for ^{7}Be to be used as a tracer of soil particle transport. In the present study, we collected throughfall, which is precipitation passing through the tree canopy, and overland flow, and measured ^{7}Be concentration in dissolved and particulate form to determine the distribution coefficient of ^{7}Be in overland flow along a forested hillslope. Additionally, we conducted batch experiments using fresh (^{7}Be-rich) rainwater and old (^{7}Be-dead) surface soil collected at the study site. K_D of ^{7}Be in overland flow along the forested hillslope was $1.2\text{-}7.6 \times 10^4$. K_Ds of ^{137}Cs and ^{210}Pb in overland flow were of the order 10^3-10^5. The percentage of ^{7}Be in particulate form depended on the sediment concentration in overland flow. Laboratory batch experiments were conducted using fresh (^{7}Be-rich) rainwater and old (^{7}Be-dead) surface soil collected at the study site. K_D of ^{7}Be was approximately $6.6 \times 10^3 - 1 \times 10^4$. These results were similar to the results for overland flow observed along the forested hillslope. For ^{7}Be, ^{137}Cs and ^{210}Pb, more than 98% were in particulate form at sediment concentrations of 10 g L^{-1}. Additional batch experiments using a high purity clay mineral showed a K_D for the clay mineral that was approximately 1-order higher than that for forest soil. These field monitoring and batch experiments confirmed that ^{7}Be is highly reactive and is primarily transported in particulate form, although a small amount of ^{7}Be in overland flow can be transported in dissolved form along the forested hillslope.

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CLASSICATION OF ORES USED FOR THE RADIATION SOURCE IN NORM BY PGAA

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NORM is **N**aturally **O**ccurring **R**adioactive **M**aterial found in consumer products. The existence of such consumer products; NORM in our environment raises the radiation exposure dose to the users. This has become a world-wide issue. The sources of NORM are mainly radionuclides in the thorium (Th) and uranium (U) series. However, we have no information about the kinds of ores are added to NORM. It is well-known that the elements of Th and U usually exist with the elements of rare earth metals. So we sought a new method for identifying in the kinds of ores added to the consumer products from the correlation of the concentration ratios of the Th/U and the Gd/Sm in NORM and ores. The conventional γ-ray spectrometry by a Ge detector for analysis of Th and U and the prompt gamma-ray activation analysis for Sm and Gd were employed. It was found that the radiation sources of NORM of the consumer products in a recent market were mainly monazite and tourmaline.

PO-1-8-6 13543

RADIOACTIVITY IN VEGETATION, VEGETABLE, AND TRANSFER OF RADIONUCLIDES FROM SOIL TO VEGETATION OF OSME NORTERN AREA OF PAKISTAN USING γ-RAY SPECTROMETRY

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The analysis of gamma emitters natural radionuclides i.e. ^{226}Ra, ^{232}Th and ^{40}K has been carried out in soil, vegetation, vegetable and water samples collected from some Northern area of Pakistan, using gamma spectrometry. The gamma spectrometry was carried out using high purity Germanium (HPGe) detector coupled with a computer based high resolution multi channel analyzer. The specific activity in soil ranges from 24.7 to 78.5 Bq/kg, 21.7 to 75.3 Bq/kg and 298.5 to 570.8 Bq/kg for ^{226}Ra, ^{232}Th and ^{40}K with the mean value of 42.1, 43.3, 9.5 and 418.3 Bq/kg, respectively. In the present analysis, potassium-40 was the major radionuclide present in soil, vegetation, fruit and vegetable samples. The concentration of ^{40}K in vegetation sample varied from 646.6 Bq/kg to 869.6 Bq/kg on dry weight basis. However, the concentration of ^{40}K in fruit and vegetable samples varied from 34.0 Bq/kg to 123.3 Bq/kg on fresh weight basis. In vegetation samples, along with ^{40}K, radium-226 and thorium-232 were also present in small amount. The transfer factors of these radionuclides from soil to vegetation and vegetable were also studied. The mean transfer factors of ^{40}K, ^{226}Ra and ^{232}Th from soil to vegetation were estimated to be about 1.91, 0.06 and 0.06, respectively. The analysis of water samples showed specific activities values for all radionuclides below detection limit. The specific activities of radionuclides found in all samples during the current investigation were nominal. Therefore they are not associated with any potential source of health hazard to the general public.

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RELATIONSHIPS AMONG ^{137}Cs, ^{133}Cs, AND K IN PLANT UPTAKE OBSERVED IN JAPANESE AGRICULTURAL FIELDS

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Cesium-137 (^{137}Cs) is a radionuclide which can be potentially released from nuclear facilities to the environment; therefore, its transfer from soil to plant is of great interest for environmental safety assessments. It is necessary to take into account the form in which Cs exists in the soil because Cs can be fixed in clay minerals and the fixed Cs is not easily used by plants. Since a stable isotope ^{133}Cs is present in the environment, plant uptake of ^{137}Cs should be the same as that of ^{133}Cs. Moreover, Cs uptake by plant is influenced by potassium (K), which is an essential element, for two major reasons; K and Cs have similar chemical characteristics, and a large amount of K is present in agricultural fields due to application of K fertilizer. In this study, we discuss relationships among ^{137}Cs, ^{133}Cs, and K in plant uptake with especial consideration of the assumptions of two fractions in soil, that is, exchangeable (plant-available) and fixed (plant-unavailable) fractions.

We used our database for soil and crop samples collected from 43 agricultural fields throughout Japan; the database contains various element concentrations in crop and soil, as well as basic soil properties such as pH, cation exchange capacity, and exchangeable K concentration. Additionally, batch sorption test and sequential extraction were carried out to determine concentrations of ^{137}Cs and ^{133}Cs in the fixed fraction in each soil sample.

Since ^{137} Cs is a fallout radionuclide, its concentration in soil had no correlation with ^{133}Cs concentration in soil. However, ^{137}Cs concentration in crop has a good correlation with concentration with ^{137}Cs in crop with Spearman's rank correlation coefficient $R_s = 0.78$ ($p < 0.01$). We saw that ^{133}Cs and ^{137}Cs were taken up by crops at a certain rate from soil regardless of how much ^{133}Cs or ^{137}Cs were included in each soil sample. For the concentration of K in the fixed fraction, there was a good correlation with that of ^{133}Cs but no correlation was found with that of ^{137}Cs. As a result, the abundance ratio between ^{133}Cs and ^{137}Cs were relatively constant in the exchangeable fraction, but not in the fixed fraction due to ^{133}Cs presence in the soil component. Details of the results will also be discussed.

ASSESSMENT OF RADIONUCLIDES, TRACE METALS, AND RADIONUCLIDE TRANSFER FROM SOIL TO FOOD OF JHANGAR VALLEY (PAKISTAN) USING GAMMA SPECTROMETRY

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The gamma spectrometric analysis of soil and essential foodstuffs e.g. wheat, millet, Potato, lentils and cauliflower, which form the main component of the daily diet of the local public, was carried out using high purity germanium (HpGe) detector. The gamma spectrometry was carried out using high purity Germanium (HPGe) detector coupled with a computer based high-resolution multi channel analyzer. The specific activity in soil samples ranged from 30.0 Bq/kg to 81.2 Bq/kg, 31.4 Bq/kg to 78.25 Bq/kg and 308.8 Bq/kg to 2177.6 Bq/kg for ^{226}Ra, ^{232}Th and ^{40}K with the mean value of 56.2, 58.5 and 851.9 Bq/kg, respectively. The average activity measured for ^{226}Ra, ^{232}Th and ^{40}K in soil samples were higher than the world average. The major radionuclide found in the foodstuffs studied was ^{40}K, while ^{226}Ra, ^{232}Th and ^{137}Cs were detected in very nominal amount. The results clearly indicate that there is no health hazard to human being from these radionuclides as they are well below the Annual Limit of Intake (ALI) of these radionuclides. The transfer factors of these radionuclides from soil to food were also studied. The mean transfer factors of ^{40}K, ^{226}Ra, ^{232}Th and ^{137}Cs from soil to food were estimated to be about 0.17, 0.07, 0.16 and 0.23 respectively. An artificial radionuclide, ^{137}Cs, was also present in detectable amount in all samples. The internal and external hazard indices were measured and had mean values of 0.70 and 0.55 respectively. Absorbed dose rates and effective dose equivalents have been determined in the present study. Trace metals such as Cr, Pb, Ni and Zn were also determined in the soil samples. The concentration of radionuclides and trace metals found in these samples during the present study were nominal and do not pose any potential health hazard to the general public.

ORIGIN OF ENRICHED URANIUM CONTAINED IN JAPANESE ATMOSPHERIC DEPOSITS

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Uranium isotope ratio, especially $^{235}U/^{238}U$ ratio, does not fractionate substantially in the nature. Anomalous $^{235}U/^{238}U$ ratios observed in environmental samples thus resulted from anthropogenic nuclear activities except from natural nuclear reactors. In the 1950s, Japan Meteorological Agency (JMA) started sampling atmospheric deposits in Japan and the measurement of anthropogenic radioactivity for monitoring environmental pollution connected to nuclear activities. The atmospheric deposits have been collected every month with rainwater using a stainless still open surface sampler with the surface area of 0.5 m^2 by JMA at its monitoring stations. The monitoring has been conducted mainly by measuring the concentrations of ^{90}Sr and ^{137}Cs as major nuclear fission products. In the present study, the chemical compositions and the isotope ratios ($^{235}U/^{238}U$) in them have been measured. The $^{235}U/^{238}U$ ratios in the atmospheric deposits collected at Fukuoka between 1964 and 2000 are slightly high compared to the natural ratio throughout the period. This is probably due to Asian mineral dust containing enriched uranium originated from nuclear test explosions conducted at the central Asia., because Fukuoka is located at southwest Japan (Kyushu Island) and, there, Kosa (Asian mineral dust) events are frequently observed in springtime. Acid insoluble fractions of the deposits, which are mainly composed of silicate minerals, also show high $^{235}U/^{238}U$ ratios compared to the natural ratio, which suggests that enriched uranium fused with silicate sands at the hypocenter have been transported by prevailing westerly wind since 1964 until today. On the other hand, since the uranium content in the deposits and its annual deposition in Fukuoka in 1964 were several times larger than those in 2000, the amount of enriched uranium deposited there in the 1960s had been larger than that in these days. As a result of principal component analysis using the weather data and the contents of minor elements in the deposits as variables, the uranium content in Fukuoka deposits in 1964 was identified as a second principal component together with ^{137}Cs and ^{210}Pb but not with lanthanides, and the one in 2000 was identified as a first principal component together with lanthanides. This suggests that the transport mechanism of uranium contained in the atmospheric deposits is different between 1964 and 2000. Based on those findings, a remarkable amount of enriched uranium might have been deposited as fallout directly from nuclear test explosions in the 1960s. Contrary to this, uranium might have been deposited as re-suspension of surface soils contaminated with enriched uranium originated from nuclear explosions in the present days.

COMPARISON OF DEEP UNDERGROUND NEUTRON FLUX MEASURED WITH A HELIUM-3 FILLED PROPORTIONAL COUNTER AND EVALUATED FROM ELEMENT COMPOSITION OR THE ISOTOPIC RATIO OF ^{36}Cl/Cl IN GRANITE ROCK

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Neutron flux in underground can be evaluated from the element composition of rock as well as by suitable counting equipment and neutron activation methods. The element composition yields several constants, such as fast neuron emission rate, neutron diffusion length, neutron diffusion coefficient and resonance escape probability, to calculate thermal neutron flux in homogeneous system. Fast neutron emission rate is evaluated from the concentration of uranium, which undergoes spontaneous fission, and the concentration of alpha emitter and light element, which induce (α, n) reaction, and the latter constants are evaluated from nuclear cross section of granite rock. In this study chlorine isotopic ratio and element composition in granite core bored in a deep underground tunnel were measured and neutron was detected with a helium-3 filled proportional counter in the borehole. The thermal neutron flux evaluated from the chlorine isotopic ratio determined by accelerator mass spectrometry and the element composition were $(3.8\pm0.5) \times 10^{-5}$ and $(4.4\pm0.5) \times 10^{-5}$ $(cm^{-2}s^{-1})$, respectively. On the other hand, the results of in-situ measurements with the proportional counter yielded (3.3 ± 0.1) x 10-5 $(cm^{-2}s^{-1})$.

The values evaluated above are in good agreement with the counting measurements, which shows that the validity of neutron flux evaluation from element composition and/or the isotopic ratio of ^{36}Cl/Cl and the stable neutron flux in underground environment for at least one million year corresponding to the period in which the activity of chlorine-36 is saturated.

STUDY OF THE ^{7}Be AND ^{137} Cs ACTIVITIES IN MUSHROOMS FROM SOUTHERN AND WESTERN FINLAND

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Edible mushrooms were collected along the coasts at many different locations in Southern and Western Finland. The were dried and the ^{7}Be and ^{137}Cs activities were determined through the intensities of the γ-lines of 478 and 661 keV, repectively, in the stable daughter nuclei ^{7}Li and ^{137}Ba. The amount of dried material was about 30 cm^{3}. Most of the activities of ^{137}Cs, with a half-life of 30.2 years, are from the Tjernobyl incident in 1986, and also from nuclear weapons tests earlier in the 1950s. On the contrary, the nuclide ^{7}Be has a half-life of only 53.3 days, and so must be generated continuously. This is achieved via the cosmic radiation, the protons of which have sufficiently high energies to produce ^{7}Be through spallation of nitrogen and oxygen in the upper atmosphere. These effects were first reported in [1], and later discussed in [2]. See also [3] for a recent example. As for a previous case of edible vegetables [4], we discuss the differences in activities between the specimen, and we also discuss the intensity differences as a function of geographical position. The largest position differences were about 550 km.

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PLUTONIUM OXIDATION STATE DISTRIBUTION IN NATURAL CLAY SYSTEMS: EFFECT OF IRON OXIDES AND MICROORGANISMS

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Plutonium oxidation state distribution at trace levels pertinent to retardation processes at an engineered barrier for a cement (concrete) based near-surface low and intermediate level radioactive waste repository, and a far-field barrier for a high level repository was studied. Triassic clay from the industrial exploitation site Šaltiškiai in North Lithuania with well defined physical and chemical properties was used in sorption experiments.

The effect of the clay coatings on the migration can vary in a wide range: from partial inhibition to substantial enhancement of radionuclide sorption to geological materials. Iron-bearing minerals showed not only sorptive but also oxidative-reductive capacity (including that biologically mediated) towards redox-sensitive radionuclides and metals, observed in the environment and proved under well defined laboratory conditions. However, oxidation–reduction reactions are of the top importance especially for actinides because of the essential influence on their speciation, solubility and transport. Clay samples with different amount and compositions of iron oxides, synthetic magnetite, goethite and hematite as well as bacteria and fungi isolated from the Triassic clay and groundwater were used in equilibrium and kinetic sorption experiments to understand the mechanism of oxidation state transformation and quantification of redox reactions.

Solvent extraction techniques (using TTA, HDEHP, DBM and PMBP), ultrafiltration and alpha spectrometry as well as ICP-MS were employed to characterize the oxidation states of the formed plutonium species.

Sorption and desorption tests using Am(III), Np(V) and U(VI) as oxidation state analogs for Pu(III), (V) and (VI) were conducted to determine appropriate condition to remove Pu from the solid-phase. Results indicated that Pu can be quantatively desorbed (up to 96±6 %) from solids, which is in good agreement with the data obtained in different laboratories using Pu oxidation state analogs and sequential extraction procedures. Additional experiments performed using ^{242}Pu(IV), ^{236}Pu(III) indicated that Pu(III) and Pu(IV) remain stable during the desorption procedure from solids.

Pu(IV) oxidation state distribution in the system of natural clay -0.1 mol·L^{-1} $NaNO_3$ after 7-day contact time) showed an increase in the concentration of Pu(III) from 10 to 20 % at pH 5 in solids. The system is characterized as carbonate-free (TOC < 10 ppb), low oxygen (< 50μ mol·L^{-1}), and low organic content (0.034% of TOC in the solids) as well as Fe(II)-and Fe(III)-bearing minerals were detected in the clay by Mössbauer spectroscopy and XRD analysis. A kinetic sorption/reduction experiment with goethite suspensions (0.01 mol·L^{-1} $NaNO_3$ containing Pu(V)) indicated the presence of Pu(III) in the solids up to 15%.

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STUDY OF Pu(IV) AND Am(III) SORPTION TO CLAY MINERALS

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Performance assessment of radioactive waste disposal requires long-term prediction of radionuclide migration through the engineered barriers and the geological environment. Understanding of geochemical processes affecting the migration and estimation of their parameters are key issues. Existing sorption data are not sufficient for prediction of Pu and Am retention by engineered barriers made of natural clays and explanation of the role of ferric oxides on the retention of Pu by natural clays. Published data showed certain variations in sorption behavior of Pu and Am this is can be an indication of Pu(III) different behavior as well. Therefore sorption of Pu(IV) on clays with different content and composition of iron minerals in their coatings was studied. In order to assess the possible effect of Pu reduction to its trivalent oxidation state, the sorption of Pu(IV) was compared with the similar sorption of Am(III) which can serve as analogue for Pu(III). In a first attempt, the sorption experiments concentrations with synthetic rain water, natural groundwater and natural clay minerals were undertaken in order to simulate conditions as close as possible to natural ones at low and intermediate waste repository when the rain water breakthrough can cause dissolution of cement and can result in the pH, ionic strength and concentration of Ca, Na, K gradients. In a second attempt, the experiments under well defined laboratory conditions with pure phases of iron oxides and humic acids naturally present in the clay mineral coatings were conducted. Sequential extraction studies carried out in combination with Mössbauer spectroscopy and XRD analysis showed that Pu was mainly bound to iron oxides while Am was more associated with the exchangeable and carbonate fractions. Mn oxides were below detection limit by XRD in the studied clay, in addition, only small amounts of Pu bound to Mn oxides were found (≤1%). Sequential extraction of Pu adsorbed on the clay has indicated that the increase in pH during the sorption results in changes of the sorption patterns of Pu (IV) and Am(III) to components of the clay. An increase in bonding of Pu and Am with organic matter was observed at high pH values. Moreover, time dependent redistribution of Pu associated with iron oxides and organic matter was observed for clay samples with low content of iron oxides as well as Pu redistribution between amorphous and crystalline iron oxides was found for samples contained mineral siderite in the coatings.

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MOLECULAR SIZE DEPENDENCY OF Am COMPLEXED WITH HUMIC AND FULVIC ACIDS IN GROUNDWATERS WITH HIGH DOC CONCENTRATION

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As colloidal organic matter, humic substances (HS) are widely recognized as important complexing ligands for trace elements in aquatic environments. The complexation of humic substances with actinide ions is not well understood because they are complex polyelectrolytes and show diverse properties depending on environmental conditions. Several researchers have identified some relationships between molecular sizes and chemical parameters such as chemical composition and functional group contents of soil and aquatic HS. The sizes and shapes of humic molecules are of fundamental importance for elucidating the many humic reactions and interactions. The objective of this study is to elucidate complexation properties of Am with humic (HA) and fulvic acids (FA) having different molecular size distribution and carbon composition. We studied the size dependence and selectivity for the Am complexation using groundwater (Mobara and Tokachi) HA and FA at neutral pH 6 and with ionic strength of 0.01 M. Complexation experiments were carried out in a medium of 0.01 M $NaClO_4$ solution at the humic concentration of 10 mg/L and pH of about 6. Ultrafiltration technique was used to size-fractionate Am in the humic solutions. Molecular size distribution of Am in the presence of HS indicates the percentage of Am associated with HS in each size fraction separated by the ultrafiltration method. Selective complexation of Am was found for the samples with molecular size ranges of 100-30 kDa for the Mobara HA and 30-10 kDa for the Mobara FA, Tokachi HA and FA. The molecular size dependency of Am may be related to the amounts of functional groups in each size fraction and/or molecular conformations of the HA and FA.

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RADIOACTIVE AEROSOL PARTICLES RELEASED FROM A PNEUMATIC IRRADIATION SYSTEM IN A NUCLEAR RESEARCH REACTOR

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Pneumatic transport system is widely used for irradiation of samples in radiation facilities such as nuclear research reactors and accelerators. In the pneumatic system, an irradiation capsule is transported through the pneumatic tube by pressured gas to irradiation positions such as reactor core, and is returned to an experiment station where high-dose radiation can be handled. Radioactive aerosols and gases are sometimes released from the pneumatic tube together with the irradiated capsule when the capsule is returned to the station.

In this paper, particle size of the released radioactive aerosol particles was investigated for the pneumatic tube of the Kyoto University Research Reactor (KUR). From the viewpoint of radiation safety, the influence of the released radioactivity was negligibly small; however, the discussion of the formation mechanism of the aerosols will aid in understanding the characteristics of radioactive aerosols in radiation facilities including high-intensity accelerators. The reactor core and the experimental station are connected with the pneumatic tube. A large part of the pneumatic tube is made of stainless steel, and only a part of the tube in the reactor is made of aluminum alloy. Compressed carbon dioxide gas is used for transportation of the capsules. The returned gas containing the airborne radioactivity was emitted from the pneumatic tube together with the returned capsules in the experimental station, and was sampled with a low-pressure cascade impactor to collect the aerosols in order to measure size distributions of the aerosols. Radioactivity of the collection filters of the impactor were measured with a Ge semiconductor detector.

The radionuclides detected in the aerosols were ^{24}Na, ^{56}Mn and several fission products such as ^{88}Rb, ^{138}Cs and ^{139}Ba. They are considered to be formed through nuclear reactions of aluminum used in the pneumatic tube in the reactor core or its minor components including impurity such as manganese and uranium. The particle size of the radioactive aerosols showed lognormal distributions with a single peak; however, the mean aerodynamic diameter was classified into two groups. The diameter was found to be ca. 0.4 μm for fission products like ^{139}Ba and 1 μm for ^{24}Na and ^{56}Mn. There are two different origins of radioactive aerosols. One is activation of non-radioactive aerosols, the other is attachment of radioactive atoms to the non-radioactive aerosols [1]. It is suggested that the 1-μm particles are formed by the activation of non-radioactive aluminum particles produced by abrasion of the inner surface of the pneumatic tube in transportation of the capsules. In contrast, the 0.4 μm particles might be formed by the attachment process of fission products emitted by recoil to radiation-induced aerosols.

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APPLICATION OF GRADED SCREEN ARRAY TO SIZE MEASUREMENT OF RADIOACTIVE AEROSOL IN ACCELERATOR ROOMS

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Aerosols are formed during an accelerator operation in the accelerator rooms and contain radioactive nuclides which are formed by nuclear reaction. Inhalation of the radioactive aerosol may be harmful to workers in accelerator facilities. The information on the size distribution is important for estimation of internal dose of the workers. A rapid measurement method is required in order to measure unstable newly-born radioactive aerosol in accelerator rooms. Diffusion battery (DB) and graded screen array (GSA) have been used to measure size distribution of radon-daughter aerosols. Generally, the DB method needs time-consuming repeated sampling to measure a size distribution. On the other hand, the GSA method needs only brief sampling. Therefore, GSA method is suitable for measurement of unstable aerosol. The GSA is composed of stacked several stainless steel screens and a backup filter. In measurement of size distributions of radioactive aerosols, the aerosols are introduced to the GSA, and are collected on the screens and the filter. The amount of aerosol particles attached to screens depends on diffusion coefficient of the particle. A smaller particle is easily collected to the screens. Activities of radioactive aerosol collected on screens were measured. The size distribution was calculated based on the number of radioactive atoms regarded as the number of particle attachment. [1] In this work, a new GSA system was developed to apply to the radioactive aerosol formed in accelerator rooms.

The performance of GSA was examined at the electron linear accelerator in the Kyoto University Research Reactor Institute. The examined GSA consisted of 100, 200, 300, 500, 635 mesh screens and a PTFE filter. Aerosol-free air was irradiated with bremsstrahlung produced by 30-MeV electron beam. The irradiated air was sampled to measure the size distribution of radioactive aerosols. The air contained ^{13}N radioactive aerosol and gas. Geometric mean diameter of radioactive aerosols formed in accelerator room was measured to be 15 to 40 nm by the DB method and 10 to 20 nm by the GSA method. The result of the GSA method was always smaller than that of the DB method. It was considered that the difference was caused by attachment of coexisting ^{13}N radioactive gas molecules to screens in addition to the ^{13}N radioactive aerosol. The attachment increased the activities on the screens. To compensate this influence a new GSA system comprising two sets of GSA was developed. The two GSAs were connected in parallel, and were used simultaneously. A PTFE filter was placed upstream of the second GSA to remove particles. Both of the radioactive aerosol and gas were collected with the first GSA, and the second GSA with the filter collected only the radioactive gas molecules attached to the screens. The net activity for the aerosol was estimated from the activity measurement of the two GSAs. Almost the same results as the DB method were obtained using the new GSA system. It was found that the new GSA system was suitable for rapid size measurement of radioactive aerosol in accelerator rooms in the presence of radioactive gas.

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STUDY ON AGGREGATION BEHAVIOUR OF HUMIC ACID: EFFECT OF pH AND ELECTROLYTE

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Migration of actinides in aquatic environment is known to be affected by the ubiquitous humic substances, owing to their strong tendency to form complexes with the actinides. Humic substances are naturally occurring organic substances that are formed randomly from decay of plant tissues and their properties depend on the ecosystem in which they are formed. As these molecules are formed from enzymatic degradation of plant polymers, they have hydrophobic organic segments and hydrophilic functional groups, which provide amphiphilic nature to these molecules. The aggregation of humic acid (HA) in solution is an important phenomenon as it not only affects its bioavailability but also determines the fate of many inorganic and organic pollutants as these organic pollutants get sequestered in the hydrophobic core of the HA aggregates. The size of HA also influences it's diffusion coefficient and thereby its mobility in the environment. The aggregation behaviour is the resultant of balance between hydrophobic interaction between organic back bone and electrostatic interactions between the charges due to deprotonation of the functional groups. Thus any change in solution conditions which affect the electrostatic interactions results in change in its aggregation behaviour. There have been conflicting reports in the literature on the aggregation behaviour of humic acid as a function of solution parameters. The aggregation behaviour of humic acid can be studied by techniques like dynamic light scattering, small angle neutron scattering, size exclusion chromatography etc. In the present work, the effect of solution parameters, namely, pH, ionic strength and cation type, on the size of HA, has been studied by dynamic light scattering. The average hydrodynamic radius of humic acid was found to be 125 ± 5 nm at pH 7. The size was found to increase from 125 to 185 nm on increasing the pH from 3 to 10, which was attributed to the deprotonation of carboxylic and phenolic groups. The increased charge on humic acid results in the swelling of the particles. The effect of ionic strength was different at pH 3 and 6. At pH 6, the initial increase in ionic strength (up to 0.1M NaCl) was found to screen the negatively charged carboxylic groups thereby reducing the electrostatic repulsions that resulted in contraction of HA particles. At pH 3, the initial decrease in size in presence of low salt concentration was not observed due to the absence of negative charges on HA aggregates. At higher ionic strengths the electrolyte acts as salting out agent thereby increasing the aggregation at both the pH 3 and 6. The intermolecular aggregation of HA in presence of bivalent ion (Ba^{2+}) was much more than that in case of monovalent ion (K^{+}), due to the ability to of the former to form intermolecular bridges.

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DEPLETED URANIUM FOUND IN THE REFERENCE FALLOUT MATERIAL FOR ACTIVITY MEASUREMENTS IN JAPAN

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The uranium isotope ratio in fallout materials reflects nuclear contamination such as dusts from nuclear weapon tests and nuclear accidents, as the natural uranium isotope ratio is practically constant. We have measured the ^{235}U/^{238}U ratios in four lots of the reference fallout material for activity measurements (RFM) prepared by Meteorological Research Institute by ICP-MS. The RFM is a mixture of monthly collected atmospheric deposition at 14 monitoring stations located all over the Japanese Islands between 1963 and 1979. The ^{235}U/^{238}U ratio was standardized against the ratio of sea water (the natural ratio), which was measured at the same time as the RFM samples. The average (^{235}U/^{238}U) sample / (^{235}U/^{238}U) seawater of the four lots of the RFM was 0.982±0.005 (90% confidence limit). We separated each RFM sample into acid-soluble and acid-insoluble fractions. About a half of uranium contained in a RFM sample was extracted into the soluble fraction. The average value of (^{235}U/^{238}U) sample / (^{235}U/^{238}U) seawater was 0.97 and 0.99 for the soluble and insoluble fractions, respectively. These results suggest that the RFM contains depleted uranium (DU) and that DU is not contained in silicate mineral particles but is mainly absorbed on them. Assuming that the DU consists of 99.8% 238U and 0.2% 235U, the DU found in the RFM constitutes about 2% of whole uranium. If we further assume that the DU was fallen out uniformly on the Japanese Islands, the amount of the DU would sum up to 0.1 mg / m^2 between 1963 and 1979. Normally, the ^{235}U/^{238}U ratios in deposition samples in Japan are equivalent to or slightly higher than the natural ratio because of the atmospheric nuclear tests carried out from 1960s to 1980s. To our best knowledge, the DU from global fallout has never been reported. It is hard to consider that the origin of the DU had been in Japan, since the first Japanese commercial plant for production of enriched uranium started its operation in 1992. The origin of the DU in the RFM still remains unsolved. However, the amount of the DU found in the RFM is, we feel, too much to ignore. The continuous endeavor to get the ^{235}U/^{238}U ratios of deposition samples at each monitoring station in each year between 1963 and 1979 is certainly needed.

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DETERMINATION OF U CONCENTRATION AND ITS ACTIVITY RATIO IN COAL AND FLY ASHES FROM PHILIPPINE COAL-FIRED THERMAL POWER PLANTS USING ICP-MS and TIMS

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The specific activity of technologically enhanced naturally occurring radioactive material (TENORM) ^{238}U and ^{232}Th in feed coal, bottom ash and fly ash samples from four major coal-fired thermal power plants in the Philippines have been measured using high-resolution gamma-ray spectroscopy system equipped with a high-purity germanium detector (HPGe). The coal and fly ash samples were digested using a microwave acid digestion method. The uranium and thorium concentrations have been determined from same samples using inductively coupled plasma mass spectrometry (ICP-MS). There was a good correlation between the measured uranium and thorium using both methods and has been estimated to be 0.97, and 0.94, respectively. The highest concentration of uranium and thorium was found for fly ash and lowest was for feed coal. The activity ratios (^{234}U/^{238}U) and ^{235}U/^{238}U were determined using a thermal ionization mass spectrometry (TIMS). This will help to understand the enhancement factor of specific radionuclides in different power plants. The activity ratio can play a major role in the migration behavior of uranium in the natural environment.

ISOTOPE RATIOS OF ^{36}Cl/Cl IN SOILS AT THE SOUTH TOHOKU BY AMS

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A long-lived radionuclide, ^{36}Cl, is produced in nature by cosmic-rays interacting with Ar in the atmosphere. However, the ^{36}Cl produced by nuclear tests between 1952 and 1958. The ^{36}Cl bomb pulse has been used as a good tracer in geoscience. We measured ^{36}Cl/Cl ratios of soil samples collected at the equal-latitude cross-sectional areas (37°20' N - 37°30' N) in the south Tohoku, Japan. ^{36}Cl/Cl depth profiles were also obtained for three sites. We developed an improved leaching process that uses diluted HNO_3 as an extractant, activated carbon to remove organic matters without decomposition, and H_2O_2 to remove residual organic matters. This sequential treatment allows us to measure selectively ^{36}Cl/Cl ratios of inorganic chlorine in soil. The isotope ratios ^{36}Cl/Cl of soil samples were determined by accelerator mass spectrometry (AMS) at the Tandem accelerator, University of Tsukuba.

We have collected 27 surface soil samples from 6 sites at the equal-latitude cross-sectional areas. The measured ^{36}Cl/Cl ratios of these samples were between 0.1×10^{-13} and 3.7×10^{-13}. Surface soil ^{36}Cl/Cl depth profiles measured at KK-12 (Kashiwazaki-Kariwa, the Sea of Japan side) and AB-1 (Abukuma, near the Pacific Ocean side) are shown in Figure. The depth profiles showed that the ^{36}Cl/Cl ratio value had higher peak at a shallow point (between 0 - 15 cm). The ^{36}Cl/Cl ratio of AB-1 (peak value was 4×10^{-13}) was two times of KK-12 (peak value was 2×10^{-13}). In the KK-12 from 15 to 100 cm depth, the ^{36}Cl/Cl ratios drop to become observed 36Cl/Cl ratio in snow at KK site and predicted ^{36}Cl/Cl ratio. But, in the AB-1 below 30 cm depth, the ^{36}Cl/Cl ratios were flat at 1×10^{-13} and were three - four times of predicted value.

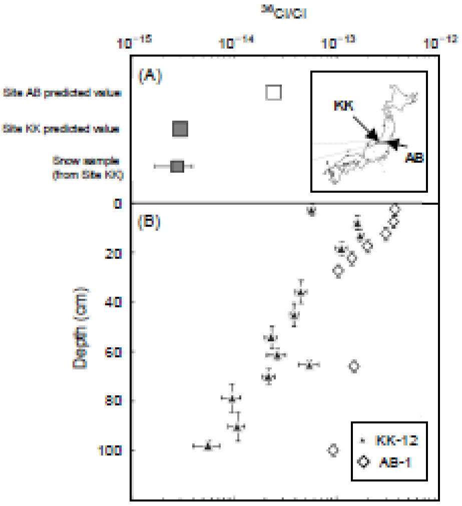

Figure Depth profiles of ^{36}Cl/Cl in KK-12 and AB-1, predicted ^{36}Cl/Cl in rainwater and observed ^{36}Cl/Cl in snow at KK site.

INTAKE OF ^{210}Po AND ^{40}K FROM THE TOTAL DAILY DIETS FOR ADULTS IN JAPANESE CITIES

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The ^{210}Po was suspected of being involved in the death of being involved in the death of a former Russian intelligence agent in 2006 in the UK. Although human exposure to this natural radionuclide in foods is estimated to be high, UNSCEAR Report 2000 does not contain data on ^{210}Po concentrations of foodstuffs in Japan. We analyzed samples of the everyday Japanese diet cooked with foodstuffs purchased at supermarkets in seven major domestic cities in 2007-2008. ^{210}Po was determined by alpha spectrometry and natural radionuclides such as ^{40}K by gamma spectrometry.
The daily intake was estimated to be 0.34-1.84 (mean±σ: 0.66±0.53) and 68.5-94.2 (81.5±8.5) Bq/d and the committed effective dose was 0.15-0.81 (0.29±0.24) and 0.16-0.21 (0.18±0.02) mSv for ^{210}Po and ^{40}K for Japanese adults, respectively, comprising a high percentage of the total exposure. The total of the mean committed effective dose for the two nuclides (0.47 mSv) was higher than the annual effective dose from ingestion of foods reported by UNSCEAR 2000 (0.29 mSv). The mean committed effective dose of ^{40}K in these major Japanese cities was comparable to the global average (0.17 mSv). The dietary exposure of Japanese adults is characterized by a higher ^{210}Po contribution than in other countries. Of the total daily dietary ^{210}Po exposure (13 food categories excluding water) for adults in Yokohama, about 70% was from fish/shellfish and 20% from vegetables/mushrooms/seaweeds, reflecting preferences of Japanese to eat a considerable amount of fish/shellfish containing high ^{210}Po concentrations.
To make the relationship between the kind of food and level of ^{210}Po intake or exposure level more clear, it would be necessary to conduct this kind of analysis for each food category involving more survey areas in Japan.

RHENIUM CONCENTRATION EFFECT ON TECHNETIUM TRANSFER THROUGH RADISH ROOTS AND RHENIUM TOXIC CONCENTRATION LEVELS IN RADISH

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Technetium-99 (^{99}Tc) is produced from the fissions of ^{235}U and ^{239}Pu with relatively high yields (about 6%) and it has a long half-life (2.11 × 105 y). Understanding its fate in the environment is important because of the potential long-term radiological consequences of releases of the radionuclide into the environment. The radionuclide is known to be concentrated in plants, and its uptake occurs not only with water mass flow or active nutrient uptake, but also with uptake of nutrient cations such as K^+ [1]. Interestingly, the uptake behavior of Tc and Re were the same so that it was implied that Re can be used a chemical analogue of Tc in plant uptake [1-3]. On the other hand, Re might affect Tc uptake when elevated amounts of Re were applied compared to Tc content. The purpose of this study to clarify the effect Re at high concentrations on Tc transfer from nutrient solution through radish plants as well as Re toxic concentration levels to radish plants instead of using Tc.

After germination, plant seedlings of radish (Raphanus sativus L.) were grown in a nutrient solution prepared from a commercially available nutrient powder, HYPONeX, which was dissolved in deionized water (1:1000 in weight). The plants were placed in a greenhouse at 21˚C and exposed to normal daylight conditions for about 20 days. Then, each plant was transplanted to a 120-mL plastic vessel containing new nutrient solution with $^{99}TcO_4$ (0.25 μM) and ReO_4 (0, 13 and 134 μM). The plant samples (N=3) were in contact with the solution through their fine roots for 3 days under normal daylight conditions. The nutrient solutions were collected at 0, 1, 2 and 3 days after transplanting and Tc and Re concentrations were measured. For plant samples, the fine roots were washed with deionized water and then the roots were gently wiped with paper towels. The plants were then separated into three parts, i.e., leaves, fleshy root and fine roots. Each sample part was weighed (wet-weight), oven-dried at 60 ˚C for 72 h and weighed again (dry-weight). The dried samples were digested with nitric acid and concentrations of 99Tc and Re were measured by ICP-MS and ICP-OES.

In the nutrient solutions, Tc and Re concentrations compared to the initial concentration were almost the same during the sampling period in all the treatments. The results suggested that no discrimination between Tc and Re even if Re concentration was much higher than Tc. Concerning the Tc and Re distribution in plants, no difference was found. Thus, elevated amount of Re, about 500 time of that of Tc, did not affect Tc uptake by the plants.

Since the behavior of Tc and Re were completely the same, Re toxicity to the radish plants were studied. After 15 days of germination, plants were transferred in nutrient solutions with 0, 63, 320, 1630 and 7860 μM of ReO_4^- In 4 days, radish plants in 7860 μM Re treatment stop growing. In 11 days, 1630 μM Re treatment plants stop growing. Details of the toxic levels of Re will be discussed at the presentation.

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DEVELOPMENT AND ANALYSIS OF A DYNAMIC COMPARTMENT MODEL TO PREDICT CARBON-14 BEHAVIOR IN RICE PADDY FIELD FOR DOSE ASSESSMENT OF ATMOSPHERIC RELEASE

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The carbon-14 is one of the critical radionuclides for the dose estimation from nuclear fuel reprocessing plant and nuclear waste disposal facility. To assess the impact on public health caused by carbon-14 released from these nuclear facilities in Japan, a reasonable estimation of internal dose from the rice ingestion is necessary because rice is a staple food. However, it is difficult to predict carbon-14 behavior by using the models which have been developed for other radionuclides, such as radioiodine or radiocesium, because the behavior of carbon in biosphere is much different from that of other elements. For example, carbon dioxide in air is fixed in a plant by photosynthesis as organic carbon and released from the plant by respiration. Therefore, we are developing a dynamic compartment model to predict carbon-14 behavior in atmosphere -rice paddy field – rice plant system and carbon-14 concentration in rice by using a migration prediction code, MOGRA. In this model, growing curves of "stem and leaf part" and "ear part" of a rice plant were fitted using sigmoid curves. The transfer coefficients between the compartments were estimated by using sub-models and parameters which describe transfer mechanisms of carbon in a rice paddy field, such as photosynthesis, translocation and respiration in a rice plant. A validation study of the model, carried out with "Rice Scenario" presented by the IAEA EMRAS (Environmental Modelling for RAdiation Safety) project, showed that the developed model can be practically used to predict carbon-14 concentration in rice. The model was also applied for hypothetical long term and short term releases of $^{14}CO_2$ from nuclear fuel reprocessing plant. In addition, parameter sensitivity analysis was carried out to pick out important transfer pathways and parameters for these releases.

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ENVIRONMENTAL MONITORING OF RADIOACTIVE AND NON-RADIOACTIVE CONSTITUENTS IN THE VICINITY OF WIPP- A CEMRC PERSPECTIVE

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The Waste Isolation Pilot Plant (WIPP), a U.S. Department of Energy (DOE) facility, is a deep geologic transuranic waste disposal site designed for the safe disposal of transuranic (TRU) wastes generated from the U.S. defense program. Initial concerns over the release of radioactive and chemical contaminants from the WIPP led to various monitoring programs, including the independent, academic-based WIPP environmental monitoring (WIPP-EM) program conducted by the New Mexico State University (NMSU) Carlsbad Environmental Monitoring and Research Center (www.cemrc.org), located in Carlsbad, NM. The mission of CEMRC is to develop and implement an independent health and environmental monitoring program in the vicinity of WIPP and make the results easily accessible to the public and all interested parties. This project was implemented during the WIPP pre-disposal phase, and is now continuing during the operational (disposal) phase. Under the WIPP-EM program constituents monitored include: (1) selected radionuclides, elements, and ions of interest in air, soil, vegetation, drinking water, surface water and sediment from within a 100-mile radius of WIPP as well as in the air exiting the WIPP exhaust shaft, and (2) internally deposited radionuclides in the citizenry living within a 100-mile radius of WIPP. All the WIPP-related programs at CEMRC are conducted independently and without direct DOE intervention. This article presents an evaluation of more than tens years of environmental monitoring data that informed the public that there is no evidence of increases in radiological contaminants in the region that could be attributed to releases from WIPP. Such an extensive monitoring program and constant public engagement is an ideal model for all nuclear waste repositories anywhere in the world.

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IODINE TRANSFER FROM AGRICULTURAL SOILS TO EDIBLE PART OF CROPS

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Iodine behavior is of interesting because the very long-lived ^{129}I (half life: 1.57×10^7 y) is often the most limiting or most critical component in low level and high level radioactive waste management due to its high mobility in the terrestrial environment. Since stable iodine can be used as a natural analogue of ^{129}I, knowledge on the distribution and cycle of stable iodine in the environment is highly useful for dose estimation from ^{129}I. To estimate internal radiation exposure pathways through food, mathematical models have been used and environmental transfer parameters have been applied in these models. Soil-to-plant transfer factor (TF) is an important parameter because a significant exposure pathway to humans is ingestion of contaminated food. Therefore, we have collected crop samples together with agricultural field soil samples throughout Japan. The crops were classifed in to 7 groups, i.e. leafy vegetables, tubers, root vegetables, fruit vegetables, leguminous, cereals (excl. rice) and brown rice. To measure stable iodine in soil and plant samples by inductively coupled plasma mass spectrometry, a simple extraction was applied [1]. About 100 mg of dried-sample were weighed into a 6 mL PFA vessel (026R, Savillex Co.). Then, 1 mL of super-pure grade 25% TMAH (TAMAPURE-AA-100, Tama Chemicals Co. Ltd.) was added and the vessel was closed tightly. The vessel was heated over night (about 12 h) at 60˚C. The sample was diluted to 50 mL with deionised water and centrifuged to obtain supernatant which contained about 0.5% TMAH for iodine measurement by ICP-MS. The method is also applicable to measure bromine concentrations. The method can successively recover ca. 100% of iodine from plant samples. For soil samples, water soluble, ion exchangeable and organically bound iodine could be extracted. Using the method, we measured 148 sets of soil and edible part of crop samples. Then TF, which is defined as the plant/soil concentration ratio, was calculated. Geometric means of TFs for fruit vegetables, 1.7E-2, was the highest among the crops groups we measured, while the lowest value of 5.9E-3 was observed in leguminous samples. In comparison, TFs of bromine was also calculated. The comparison results between TFs of iodine and bromine will be discussed.

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MEASUREMENT OF RADON GAS, GAMMA-RAY EXPOSURE AND SOME NATURALLY OCCURRING RADIONUCLIDES

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In the survey conducted for the study of residential radon exposures and lung cancer incidents targeting the provinces located in three different regions of Thailand [1],[2],[3], we measured indoor radon concentration and gamma-ray exposure in about 60 houses in each province. The results clearly indicated that the lowest average levels of both indoor radon concentration and gamma-ray exposure were at Khon Kaen, a province located in northeastern Thailand. We had proceeded to find the reason behind this scenario. The result of gamma-ray spectroscopic analysis of soil samples collected from the three provinces revealed that the sample from Khon Kaen yielded quite low concentrations of both Radium-226 and K-40. We postulated that these should be the cause of the generally low levels of indoor radon concentrations and gamma-ray exposures found in that vicinity. The result of this finding may also help explain the generally low yield of vegetation in those areas.

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A STUDY OF 32P-PHOSPHATE UPTAKE IN A PLANT USING A REAL-TIME RI IMAGING SYSTEM

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It is very important to visualize the process of nutrient absorption and distribution to study physiological activity of the plant. Therefore, we developed real-time radioisotope (RI) imaging system, where RI tracers were applied to the plant sample. This system allowed the quantitative measurements concerning the uptake of nutrients labeled with isotopes, such as ^{45}Ca, ^{35}S, ^{32}P and ^{14}C, as long as several days. The beta-rays emitted from the sample were converted to light by a CsI(Tl) scintillator and were guided to a highly sensitive CCD camera. The front of the scintillator was covered with an Al plate with different thickness so that the plate shield well the LED light and allow to penetrate the selected beta-rays with relatively high energy. We employed *Lotus Japonicus* for the sample plant and observed the behavior of ^{32}P-phosphate absorbed from roots in culture solution as well as translocation movement to above-ground part of the plant. The environment of daytime and night was simulated by the ON/OFF of LED timer and the difference of the ^{32}P-phosphate accumulation in roots and leaves during daytime and night was analyzed. The accumulation of ^{32}P-phosphate in leaves was highly dependant on light irradiation, whereas the absorption from root was indifferent to light. The transfer function of phosphate within the plants during the developmental stage was obtained from the analysis of ^{32}P uptake images. We are now trying to get isotope specific moving image when two kinds of isotopes, such as ^{32}P and ^{35}S, were applied at the same time to the plant, through an image analysis.

INTERACTION OF PLUTONIUM WITH MONTMORILLONITE: SURFACE COMPLEXATION AND ION EXCHANGE

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Due to their abundance, aluminosilicate minerals are proposed to play an important role in retarding actinide subsurface migration. In this work, sorption of Pu(IV) and Pu(V) to silica, gibbsite, and Na-montmorillonite was examined as a function of time and pH. To infer ion exchange behavior, batch sorption experiments were performed to examine Np(V) and Pu(V) interactions with montmorillonite in solutions ranging from 1 to 1000 mM NaCl.

Based on observed sorption behavior and measurements of the plutonium oxidation states, the systems appear to reach a steady state where plutonium associated with the solid phase is predominantly Pu(IV) and aqueous plutonium is predominantly Pu(V). A surface complexation model assuming monodentate surface complexation between Pu(V) and Pu(IV) and aluminol and silanol sites was developed using the gibbsite and silica sorption datasets. Based on the observation of aqueous Pu(V) in systems which were initially Pu(IV), oxidation of Pu(V) by dissolved oxygen was included in the model and constrained with redox potential measurements. This allowed for a coupled redox/surface complexation model which is proposed to more accurately represent Pu chemistry at the mineral-water interface. This model was used to predict sorption of Pu to Na-montmorillonite assuming surface complexation with aluminol and silanol sites at clay particle edges. A reasonable prediction of Pu(V) sorption to montmorillonite was obtained across the pH range 4 to 9. However, the model failed to predict sorption of Pu(IV) at low pH values. An acceptable fit to the Pu(IV) sorption data was only achieved by assuming ion exchange of hydrolyzed Pu(IV) species.

In experiments examining the effect of ionic strength (1 to 1000 mM NaCl), the rate of Pu(V) sorption was inversely related to NaCl concentration and inversely related to pH. Little sorption of Np(V) was observed across the pH range 3 to 7. The difference in sorption behavior of Np(V) and Pu(V) is thought to be due to reduction of Pu(V) to Pu(IV). The data support a surface mediated reduction/ion exchange process within the smectite interlayers which controls plutonium sorption to montmorillonite in low pH systems.

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ESTIMATION OF THERMAL NEUTRON FLUX IN PET CYCLOTRON ROOMS BY MEANS OF RADIOACTIVE ANALYSIS OF BOLTS IN THE ROOMS

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Recently, the number of the positron emission tomography (PET) examinations has greatly increased. As positron emission nuclides for the PET examination have short half-lives, they are mainly produced using on-site cyclotrons. Significant quantities of neutrons are generated with the operation of the cyclotrons. The neutrons have potential to activate the materials around the cyclotrons and cause exposure to the staff. To evaluate the neutron fluxes is one of the measures to achieve radiation safety on maintenance the cyclotrons, to assess the amount of the radioactive wastes, and to estimate the exposures. The purpose of this study is to assess the feasibility of estimating the neutron fluxes in cyclotron rooms by means of radioactive analysis of bolts in the rooms. Investigation was performed on four PET cyclotrons at facilities around Nagoya region in Japan. Several bolts in the rooms were removed to analyse both the activities and the elementary compositions. The activities were measured with a high purity Ge (HPGe) detector. The compositions were analysed using a fluorescent X-ray spectroscopy, an electron probe micro analyzer, and/or an inductivity coupled plasma atomic emission spectrometer. The neutron flux, φ (cm-2 s-1) was estimated using an equation (1).

$$\phi = \frac{A}{KN\sigma \cdot 10^{-24} \cdot \sum_i (1-e^{-\lambda t_i})e^{-\lambda T_{wi}}}, \qquad (1)$$

where A (Bq) is the activity of an induced radionuclide in a bolt, K is the abundance ratio of the target nuclide, N is the number of the atoms of the target element in the bolts, σ (barn) is the thermal neutron cross section, λ (s-1) is the decay constant of the radionuclide, t_i (s) is the operation time at the i-th operation, and T_{wi} (s) is the time from the end of the i-th operation to the measurement of the activity. To evaluate the thermal neutron fluxes in the cyclotron rooms, Au foil activation method was carried out.

When ^{18}F was produced, the neutron fluxes in the rooms were evaluated $2\sim9\times10^{5}$cm^{-2}s^{-1}. In the brass bolts, ^{69m}Zn, ^{65}Zn, ^{64}Cu, ^{58}Co, and ^{60}Co were detected. In the iron bolts, ^{56}Mn, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{69m}Zn, and ^{65}Zn were detected. In the stainless bolts, ^{58}Co, ^{60}Co, ^{56}Mn, ^{54}Mn, and ^{59}Fe were detected. The neutron fluxes estimated from the activity of ^{56}Mn in the iron bolts agreed with those evaluated by the Au foil activation method within 25% differences. Neutron fluxes estimated from the other nuclides were 1.2~2.4 times higher than those evaluated from the Au foil method. Since the half-life of ^{56}Mn is short as 2.6 h, the remaining activity in a bolt reflects only the last operation. The each Au foil was irradiated at an operation that was actually the last operation. Therefore the neutron fluxes estimated from the activities of ^{56}Mn agreed with those evaluated by the Au foil method. The other radionuclides reflected the operations from the past several times to several years. That should be one of the reasons of the differences of the neutron fluxes between from radioactive analysis of the bolts and from Au foil method. Another reason of the differences may be that there were certain quantities of neutrons with relatively high energy in the rooms. One of the further assignments is to reduce the differences by performing more precise analysis. Usually, there are a lot of small size bolts and/or screws in those cyclotron rooms and removing and analysing them are not so difficult. The analyses will bring us effective information of the neutron fluxes in the rooms. Consequently, the neutron fluxes in the PET cyclotron rooms were about $10^{5}\sim10^{6}$ cm^{-2}s^{-1}, when ^{18}F was produced. Radioactive analyses of the bolts in the rooms were helpful for estimating the neutron fluxes in the rooms.

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A NEW PREPARATION METHOD FOR NEUTRON MONITOR USING INK-JET PRINTER

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Various methods and instruments for neutron monitor have been proposed to date, fission chamber, scintillation detector, activation analysis, etc. In the case of monitoring neutrons in irradiation holes of research reactors, activation analysis method is most convenient because placing and retrieving monitor materials is easy. Metallic wires and foils are often used as monitor materials in the activation analysis method. Monitor materials are transported to neutron irradiation holes by such as pneumatic transport tubes. After neutron irradiation at an irradiation hole, activated monitor materials are sent back to a laboratory room. A neutron flux can be determined by measuring activities of the irradiated monitor materials. But, self-absorption effect causes unequal activation in neutron irradiation in using a metallic wire as a monitor material. In addition, self-shielding effect causes incorrect gamma-ray measurement. In the case of using metallic foils, those effects are ignorable because of their thinness, but difficult handling of thin foils could induce experimental error.

In this work, a new preparation method for a neutron flux monitor using an ink-jet printer has been developed. Metal solution is applied on a paper sheet using an ink-jet printer to prepare a neutron monitor material. The prepared monitor is thin enough to ignore the self-absorption and self-shielding effect, and it is easy to handle compared with a metallic foil. Neutron flux distribution at irradiation holes, guide tubes and other neutron irradiation facilities can be observed using the prepared neutron monitor, if the performances of the prepared neutron monitor, such as uniformity of applied metal and reproducibility, are confirmed.

The neutron monitors were prepared by the developed method using a standard gold solution as monitor materials. For checking the uniformity, the amount of gold applied to the print sheet was determined by neutron activation analysis (NAA) using the research reactor HANARO for several prepared monitors. The amount of gold contained in the monitor corresponds to each other within two-sigma, and the uniformity of gold applied on a paper sheet was confirmed. The correlation between the amount of the applied gold and the input parameters of the concentration for ink-jet printer was examined by NAA method. There is not linear correlation between the amount of gold and the concentration parameter. This nonlinear correlation might be caused by driver software of the ink-jet printer. But it was found that the amount of applied gold can be controlled by using the obtained correlation as calibration parameters.

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DOSIMETRY OF COSMIC RADIATIO I THE UPPER ATMOSPHERE BASED O THE MEASUREMETS AT THE SUMMIT OF MT. FUJI

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Earth is constantly bombarded by high-energy cosmic ray particles. These particles hit atmospheric nuclei and produce numerous secondary particles. Some secondary ions help forming clouds that reflect sunlight back into outer space, which could change the climate of the Earth. Since the Sun forms a shield against galactic cosmic rays (GCR) entering the heliosphere, the amount of GCR produced ions should be affected by solar activity. Now, many people are interested in the relationship between cosmic radiation intensities in the upper atmosphere and the possible climate change of Earth. Cosmic radiation environment at high altitude is also in great concern for aircraft crew in view of radiological protection. The crew is repeatedly exposed to elevated levels of cosmic radiation composed of energetic protons, neutrons, electrons, photons, pions and muons. The International Commission of Radiological Protection (ICRP) [1,2] has thus recommended that exposures to cosmic radiation in the operation of commercial jet aircraft be part of occupational exposure. In Japan, assessments of cosmic radiation exposure of aircraft crew have started from the 2007 fiscal year, according to the guideline settled on at April 2006 by the Radiation Council of the Japanese government. In the assessments, cosmic radiation doses received at high altitude have been numerically calculated using transport models, because of the complexity of the radiation field in the upper atmosphere and also technical difficulties of using large monitoring instruments in aircraft. In order to secure the reliability of the assessment, however, verification by measurement is no doubt necessary. Accordingly, we have carried out cosmic radiation measurements in a facility of the Mt.Fuji Weather Station located at the summit of Mt. Fuji (3,776 m in altitude; the highest position in Japan) during the summer of 2008/2009 to check the accuracy of numerically predicted values. The results obtained with several types of neutron monitor [3], scintillation detector [4] and ionization chamber coupled each with an exclusive data logger showed good agreements with advanced model calculations [5]. It is therefore considered that, with support by such continuous radiation monitoring at a high mountain, we can reliably estimate cosmic radiation dose rates in the upper atmosphere (>10km) under quiet solar conditions.

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ADVANCEMENTS IN BURN-UP MEASUREMENTS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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The typical burn-up monitor for nuclear fuel characterization has been Nd-148. This analysis was accomplished using isotope dilution thermal ionization mass spectrometry (ID-TIMS). This work will evaluate the application of inductively coupled plasma mass spectrometry (ICP-MS) for the characterization of various nuclear fuels for alternative burn-up monitors. The ICP-MS's multi-element capability will be utilized to analyze the fuel samples for multiple fission products. An exhaustive determination of the fission products in the nuclear fuels will enable the selection and rejection of numerous fission products due to dissolution problems, isobaric interferences or polyatomic interferences. In addition to the use as a burn-up monitor, certain fission products will be discussed in terms of nuclear forensics, nuclear modeling as well as other pertinent applications. The use of the multiple fission product monitors as well as the contribution of experimental uncertainties will also be discussed.

CHANGE OF ELECTRON CAPTURE DECAY RATE IN A COMPACT MEDIUM

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It is known from the earlier works that the decay rate of electron-capturing ^{7}Be changes a little bit [1,2,3] (maximum observed change ~1%) in different chemical environments. These results have been understood in terms of the electron affinity and lattice structures of the host media causing a change of the number of valence 2s electrons and hence the electron density at the nucleus. Quantitative calculations using density functional code have also been performed [2,3]. Since only s-electrons can have significant overlap at the nucleus and this overlap also drops rapidly for higher orbital s-electrons, no significant change of decay rate in different environments was generally expected for higher atomic number electron-capturing nuclei. It was also observed that the decay rate of an electron-capturing ^{7}Be nucleus embedded in a lattice can be increased by applying external pressure [4]. So it would be interesting to study the change of electron capture decay rates of large electron-capturing radioactive atoms such as ^{109}In and ^{110}Sn implanted in small Au lattice (lattice length = 4 Angstrom) compared to those in a larger Pb lattice (lattice length ˜ 5 Angstrom). Due to the spatial confinement, the eigenstate energies of the implanted atom would increase and this should increase the electron density of the orbital electrons at the nucleus, increasing the decay rate of an electron capturing radioactive nucleus. So, the electron capture decay rates of large atoms such as ^{109}In and ^{110}Sn should be faster in Au compared to those in Pb. We measured the change of half-life of the electron capturing ^{109}In ($\tau_{1/2} \approx 4.2$ hours) and ^{110}Sn ($\tau_{1/2} \approx 4.2$ hours) nuclei implanted in Au, Al and Pb. These radioactive nuclei were produced by bombarding a 10.7 mg/cm^{2} thick niobium foil with a 150 MeV ^{20}Ne beam from the Variable Energy Cyclotron Centre, Kolkata, India and implanted in either a gold or aluminum or lead catcher foil. After each implantation run, the foil with the implanted radioactive ions was cooled for an hour to get rid of all short-lived radioactive nuclei. Then the gamma radiation from the foil was measured by placing it in front of a four-segmented CLOVER detector manufactured by Canberra-Eurisys. In order to correct for the dead time of the measurements and other systematic errors, a ^{60}Co source ($\tau_{1/2} \approx 5$ years) was placed at a fixed distance from the detector assembly. The ratio of 203 keV γ-ray from ^{109}In and the sum of 1173 keV and 1332.5 keV γ-rays from ^{60}Co was monitored with time and a similar ratio was monitored for ^{110}Sn. We have observed [5] that the orbital electron capture rates of ^{109}In and ^{110}Sn increased by (1.00 ±0.17) % and (0.48 ±0.25) % respectively when implanted in the smaller Au lattice compared to implantation in a larger Pb lattice. The electron capture rates in Au and Al lattices have been found to be about equal because of the similar lattice sizes of Au and Al. These observations are interpreted to be a result of the higher compression experienced by the large radioactive atoms in the smaller spatial confinement of the Au and Al lattice. We have also developed a simple model to explain these observations.

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RECENT DEVELOPMENTS IN HEAVY ELEMENT SEPARATION METHODS USING DGA RESIN

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A new separation scheme for Db is being investigated based primarily upon Eichrom's DGA (N,N,N',N'-tetra-n-octyldiglycolamide (DGA Resin, Normal) or N,N,N',N'-tetrakis-2ethylhexyldiglycolamide (DGA Resin, Branched)) products. Using Nb, Ta, and Pa tracers the chemical differences between these elements in this system have been studied. Decontamination factors from actinide species and Rf homologs have been measured. How small of a separation system can be effectively utilized in accelerator-based experiments has been studied. Minimizing the scale of the chemical process allows the system to be performed as rapidly as possible, permitting greater flexibility in the range of half-lives that can be accessed by this liquid chemical system. Automation of the process is proceeding, which will allow the experiment to perform with minimal operator interaction. The system being created will permit other single-column chemistries to be employed with minimal system re-work. Dual column chemistries can be employed providing that the eluant from the first column is the load solution for the second, or can easily be changed with a mixing tee.

PREPARATION OF 248Cm TARGET FROM OLD 252Cf NEUTRON SORCE

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An isotope of ^{248}Cm is useful as a target material for a production of trans-actinide nuclides and for a chemical study of Rf, Db, Sg and Hs, because this curium isotope has a large atomic number, a high neutron to proton ratio and a long half-life. It can be produced by a neutron capture process using a high-flux nuclear reactor. However, the ^{248}Cm has not been provided in Japan and expensive one must be purchased from abroad. A convenient way to solve the problem is to isolate ^{248}Cm as a decay product of ^{252}Cf [1], which were used as neutron sources. If ^{248}Cm can be separated from old ^{252}Cf neutron sources, it is possible to make a ^{248}Cm target in Japan.

We obtained old ^{252}Cf neutron sources as a Cf(Cm)-Pd cermet wire in a stainless steel container. At first, it was taken out from the container by a pipe cutter and solved in aqua regia. Then, the Cf(Cm) was separated from the Pd and most fission products by a hydroxide precipitation method and an anion ion-exchange method. A mutual separation of the Cm/Cf was performed by the use of an anion exchange method with a mixture media of nitric acid and methyl alcohol. This method has a lot of advantages to use as an eluent for mutual separation and for target preparation by electrodeposition, because of its low viscosity, low boiling point and lesser content of impurities [2, 3]. The ^{248}Cm target of 0.48 mg/cm^2 thickness was prepared by electrodeposition onto beryllium backing foils of 2.0 mg/cm^2 thickness after purification of each target material by ion-exchange methods. The isotopic composition was ^{248}Cm 87.30%, ^{246}Cm 11.83%, ^{245}Cm 0.85%, and ^{244}Cm 0.02%.

The 94.1 MeV $^{18}O^{6+}$ beams of approximately 350 particle nA accelerated by the RIKEN K70 AVF Cyclotron were irradiated on the prepared ^{248}Cm targets. The reaction products of ^{261}Rf were transported by the He/KCl gas-jet method through the Teflon capillary to a rotating wheel system for measurement of α decays, where the transported products were deposited on thin Mylar foils. The foils were periodically rotated to position the products between seven pairs of Si PIN-photodiodes for α-particle measurement. At the same time as producing the ^{261}Rf, the background condition due to transfer products of ^{211m}Po and ^{214}At was investigated.

In this conference, preparation of ^{248}Cm target, including the ^{248}Cm/^{252}Cf separation and electrodeposition of the ^{248}Cm, and irradiation test are reported.

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AVERAGE EQUILIBRIUM CHARGE STATES OF SUPERHEAVY RECOIL IONS MOVING IN A DILUETE HELIUM GAS

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A gas-filled recoil separator at RIKEN (GARIS) has been used as a powerful tool for superheavy element (SHE) study, including SHE chemistry.

One of the most important parameters for an operation of GARIS is an average equilibrium charge states q_{ave} of recoil ions moving in a filled gas. We have systematically measured the q_{ave} of heavy ions (^{169}Tm, ^{208}Pb, $^{193,\,209}$Bi, ^{196}Po, ^{200}At, $^{203,\,204}$Fr, ^{212}Ac, ^{234}Bk, ^{245}Fm, ^{254}No, ^{255}Lr, and ^{265}Hs) moving in a helium gas by using GARIS. As a result, we derived an empirical formula on $q$ave of heavy ions in a helium gas (see blue broken line in Fig. 1) [1] as a function of the velocity and the atomic number of an ion on the basis of the Tomas-Fermi model of the atom [2]. The formula was found to be applicable to search for SHE nuclides of ^{271}Ds, ^{272}Rg, ^{277}112, and ^{278}113 produced by cold fusion reactions. Recently, we have also investigated the performance of GARIS for actinide-based hot-fusion reactions, ^{238}U(^{22}Ne,5n)^{255}No, ^{248}Cm(^{18}O,5n)^{261}Rf, ^{248}Cm(^{22}Ne,5n)^{265}Sg, and ^{248}Cm(^{23}Na,5n)^{266}Bh. As a result, it is found that a different empirical formula on q_{ave} should be used for the prediction of q_{ave} of hot fusion products (see red broken line in Fig. 1). The average equilibrium charge state, transmission of GARIS, and background conditions obtained in hot fusion studies were compared with our previous data taken for cold fusion studies.

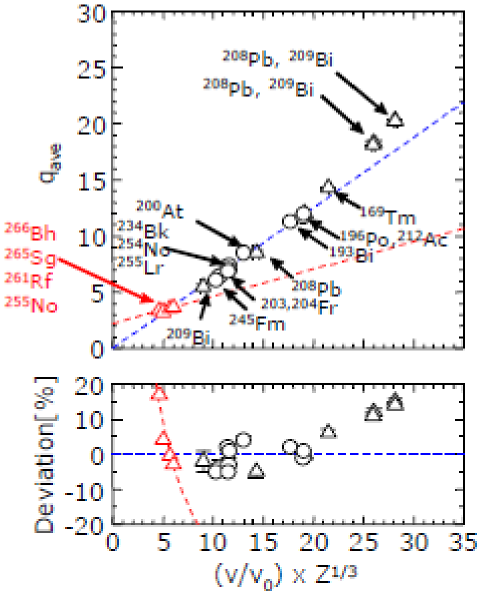

Fig. 1: (Upper part) Systematics of the measured equilibrium charge state q_{ave} of heavy recoil ions moving in a dilute helium gas. Blue broken line: $q_{\text{ave}}=0.625\times(v/v_0)\times Z^{1/3}$, red broken line: $q_{\text{ave}}=0.242\times(v/v_0)\times Z^{1/3}+2.19$. (Down part) Deviation of q_{ave} from ones predicted by $q_{\text{ave}}=0.625\times(v/v_0)\times Z^{1/3}$.

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PRECISION MEASUREMENT OF THE HALF-LIFE OF ^{196}Au AND ^{202}Tl

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Half-lives for many isotopes are known with relatively small uncertainties. However, these values are not always in agreement with a result of a new experiment. As the statistical error becomes smaller, other experimental errors become more important. For the estimation of these errors, it seems to be valid to compare the results of the measurement where many samples and/or deferent detectors are used. In this study, the half-lives of ^{196}Au and ^{202}Tl were measured using many sources with several Ge detectors.

The sample production was performed at the Laboratory of Nuclear Science, Tohoku University. The ^{196}Au and ^{202}Tl were obtained from the (γ, n) reaction of ^{197}Au and ^{nat}Tl. A gold foil and Tl2O3 powder were irradiated with bremsstrahlung photons produced by the 30-MeV electron beam impinging on a platinum target. The irradiation was done at the electron beam current of about 135μA for several hours. The half-lives of ^{196}Au and ^{202}Tl were determined from the decay curves measured using automated sample changers. Each automated sample changer consists of a high-purity Ge detector and two sample arms driven by a stepping motor. The gamma spectra for each sample were accumulated for 3550 seconds every 2 hours by the multi-channel analyzer ORTEC TRUMPTM card. The decay curves were followed during several half-lives. The time clock of the data acquisition system was calibrated every 10 minutes using the Japan standard time which is distributed via a long-wave radio signal. In order to estimate the dead time of the data acquisition system, we employed the reference-source method with a ^{137}Cs source, where the activity ratio (R) of the sample to that of the ^{137}Cs reference source was followed. In this method, the half-life is given as $T_{1/2}=1/(1/T'_{1/2} - a/\ln 2)$, where $T'_{1/2}$ is the half-life of the reference sample, a is the slope in lnR vs time. At the conference, the detailed experimental procedure and the results will be presented.

PRECISION MEASUREMENT OF THE HALF-LIFE OF ^{90m}Nb AND ^{99m}Tc

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The goal of our research is to clarify the effects of chemical structure on the decay constants of ^{90m}Nb and ^{99m}Tc. Almost all ^{90m}Nb and ^{99m}Tc nuclei decay via a 2.3-keV transition from the 124.7-keV level to the 122.4-keV level in ^{90}Nb and a 2.2 keV from the 142.7 keV to the 140.5 keV in ^{99}Tc [1], respectively. Because of the high internal conversion coefficient and low transition energy, the probability of the transition is expected to vary with changes in the chemical structure affecting the electron density at the nucleus.

In the previous studies, the decay constant of ^{90m}Nb was obtained with a radioactive equilibrium method [2] or a direct half-life measurement [3]. However, it appears that strong activities from undesired nuclear reaction products interfered with the measurements. In order to determine the short half-lives of ^{90m}Nb in various chemical states precisely, we employed an on-line gas-jet transport system in this study.

The isotope ^{90m}Nb was produced in the nuclear reaction ^{nat}Zr(p, xn)^{90m}Nb with a 14 MeV proton beam delivered from the RIKEN K70 AVF Cyclotron. Five $^{nat}ZrO_2$ targets of about 100 μg cm^{-2} thickness were prepared by electrodeposition onto an 810 μg cm^{-2} aluminum backing foil. The targets were placed in a gas-jet chamber at intervals of 8 mm. The beam intensity was about 8 μA. The proton beam entered the target stack had an energy of 13.8 MeV. The reaction products recoiling out of the targets were stopped in the helium gas (~ 100 kPa), attached to KCl aerosol particles generated by sublimation of KCl powder at 640 °C, and continuously transported to a chemistry laboratory.

The reaction products were deposited on a polyethylene terephthalate film to measure the half-life of ^{90m}Nb. After deposition for 30 s, they were dissolved in various solutions and subjected to γ-ray spectrometry. The accumulation of γ-ray spectrum for 6 s was started within 1 min after the end of the aerosol deposition and then repeated 15 times successively. In order to achieve adequate statistical precision, the procedure was repeated 120 times. The half-lives of ^{90m}Nb were determined by the reference source method using ^{137}Cs.

The peaks of ^{90g}Nb($T_{1/2} = 14.6$ h), ^{90m}Nb, ^{52m}Mn (21.1 min), ^{54m}Co (1.48 min), ^{64}Ga (2.63 min), and ^{91m}Y (49.7 min) are observed in the spectrum. The γ-peak of ^{90m}Nb at 122 keV is clearly separated from the peak of ^{90g}Nb at 133 keV, which is the closest to that of ^{90m}Nb. No serious background was observed in the γ-ray spectrum for determination of the half-life of ^{90m}Nb. The present system will allow us to measure the half-life of ^{90m}Nb with various chemical states. The results of ^{99m}Tc will be also presented at the conference.

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DEVELOPMENT OF AN ON-LINE LIQUID SCINTILLATION α-PARTICLE DETECTION SYSTEM FOR AQUEOUS CHEMICAL STUDIES OF SUPERHEAVY ELEMENTS

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Investigation of chemical properties of superheavy elements with atomic numbers $Z \geq 104$ requires an on-line rapid chemical operation and highly efficient α-particle detection due to their short half-lives and extremely low production rates. The purpose of this work is to develop an on-line α-particle detection system for aqueous chemistry of superheavy elements. Our group has employed a liquid scintillation counter (LSC). In order to apply the LSC to the detection of low rate events from superheavy elements, reduction of background signals from βparticles is required. A method to suppress βsignals based on the difference between the range of αand βparticles by using PFA tubes with hundreds μm i.d. has been developed [1]. In this study the method has been applied to a flow-type LSC for on-line experiment to detect ^{213}Fr which is produced with an accelerator.

The flow-type LSC was prepared by setting a coiled detection cell of 500 μm i.d. PFA tubes in PERALS® spectrometer. The isotope ^{213}Fr ($T_{1/2}$ = 35 s, E_{α}= 6.78 MeV) was produced by decays from the ^{209}Bi(^{16}O, 4n) reaction products with the AVF cyclotron at the Research Center for Nuclear Physics, Osaka University. The ^{209}Bi target of 315 μg/cm^2 thickness was prepared by vapor deposition on a titanium backing foil of 2.2 mg/cm^2 thickness. The ^{16}O beam entered the target material at the energy 109 MeV. The beam intensity was approximately 110 pnA. Reaction products recoiling out of the target were transported to a chemistry laboratory by a He/KCl gas-jet transport system. The transported products were collected on a dissolving unit for 1 minute and dissolved in 30 μL of water with a syringe pump at a flow rate of 1366 μL/min. They were mixed with Ultima Gold AB® in 20% of water content by volume by using a magnetic stirrer. The solution of reaction products was pumped into the coiled detection cell. After measurements for 3 min, the sample solution was drained off. The sequence of these procedures was automated and repeated by Lab VIEW system. On-line detection of αparticles of ^{213}Fr has been successfully done and βsignals overlapping with αsignals in high-energy region has been suppressed.

Additionally, we are planning to use RIKEN Gas-filled Recoil Ion Separator (GARIS) as a pre-separator to eliminate a large amount of unwanted α- and β-emitting nuclei from the reaction products for the detection of superheavy elements with LSC. The usefulness of the LSC combined with a gas-filled separator was shown by SISAK [2]. In order to estimate the background, reaction products of ^{248}Cm(^{18}O, x) reaction transported by GARIS/gas-jet system [3,4] have been measured with PERALS®. Low background measurements and the detection of ^{261}Rf have been achieved. A new LSC-chamber will be designed based on the results.

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CHEMICAL EQUILIBRIUM IN ATOM-AT-A-TIME CHEMISTRY

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Chemical studies of the heaviest elements are extremely interesting and challenging subjects in modern inorganic and nuclear chemistry. A most important and fascinating aspect is to determine the chemical properties of newly-synthesized elements at the uppermost end of the periodic table. The heaviest elements above element 100, fermium (Fm), however, must be produced at accelerators in heavy-ion - induced nuclear reactions and are available as short-lived isotopes only in quantities of a few atoms at a time. In addition, each available atom should be chemically equilibrated rapidly within its life-time. Such restricted experimental conditions make it remarkably difficult to characterize chemical properties of the heaviest elements.

We have studied liquid chromatographic behavior of the transactinide elements Rf and Db with the rapid chemical separation apparatus AIDA that enables us to perform cyclic column chromatographic separations of short-lived nuclides in aqueous solution and automated detection of α-particles within a typical cycle of 1-2 min. For the chromatographic separation, the micro-columns, such as 1.6 mm i.d. × 7.0 mm long and 1.0 mm i.d. × 3.5 mm long, are employed for the measurement of distribution coefficients (K_d) of the heaviest elements. Chemical reaction should reach equilibrium even in the micro-column.

In the experiments with AIDA, however, we measure only adsorption probabilities of Rf and Db on resin because it is quite difficult to measure elution curves of the short-lived nuclides based on an atom-at-a-time scale. Thus, we transform the observed adsorption probability value into K_d by assuming that the kinetics in the complex formation and ion-exchange chromatographic processes of the transactinide elements are as fast as those of homologues [1, 2]. We discuss the above method to evaluate reliable K_d from the adsorption values in various complexation systems.

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RADIOCHEMICAL STUDY OF SUB-BARRIER FUSION HINDRANCE IN ^{19}F + ^{209}Bi REACTION

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Unexpected steep fall-off of fusion cross sections has recently been observed in heavy-ion fusion reactions at deep sub-barrier energies. [1] Such unexpected steep falloff of fusion cross sections, so-called sub-barrier fusion hindrance, was studied experimentally and theoretically [24]. However, the mechanism of sub-barrier fusion hindrance is still an open question. Sub-barrier fusion hindrance has been studied mainly in medium-heavy mass systems because the improvement of the instruments to detect fusion residues, for example, the Fragment Mass Analyzer [5], made it possible to determine fusion-evaporation cross sections in sub-millibarn level precisely. In contrast, a limited number of studies were carried out in heavy-mass systems in which fused nuclei decay mainly not by neutron evaporation (fusion-evaporation reaction) but by fission (fusion-fission reaction). [4] In this work, the fusion-fission cross sections for ^{19}F + ^{209}Bi at sub-barrier energies were determined by a radiochemical method in order to study sub-barrier fusion hindrance in heavy-mass systems.

The irradiations of the ^{209}Bi target with 83-135 MeV ^{19}F ions were carried out at the JAEA tandem accelerator. Fission fragments were collected in the backing and the catcher foil of aluminum. After irradiation, the target, the backing and the catcher foil were dissolved in 6M HCl solution. The radiochemical separations of molybdenum (VI) from fission product mixture were carried out by using ion-exchange techniques. Precipitation of Mo with α-benzoin-oxime was applied to the preparation of samples for γ-ray spectrometry. The chemical yields were determined to be 49-80% by neutron activation analysis. The neutron activations of the samples and standards were performed at the JRR3 research reactor of JAEA.

The fission cross sections were obtained from the cross sections of ^{99}Mo by using the fractional yield of ^{99}Mo to the total fission yield which was deduced from the mass yield curves because the mass yield curves were insensitive to the beam energies. The fusion-fission excitation function for F + Bi at sub-barrier energies was determined down to nearly two order magnitude smaller than the data measured in the energy range of 88-123 MeV by silicon surface barrier detectors. [6] We will discuss the sub-barrier fusion hindrance in the present reaction, comparing the theoretical calculations [3, 7, 8] and the systematics. [2]

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CROSS-SECTION MEASUREMENTS FOR MONOENERGETIC NEUTRON-INDUCED REACTIONS AT RCNP

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The detection of long-lived and stable nuclides produced by cosmic rays in meteorite and planetary materials is essential for cosmic-ray exposure age determinations. These ages are needed to understand of the formation process of these materials. To obtain accurate cosmic-ray exposure histories, we need accurate production rates, which in turn require reaction rates for all processes that produce a specific cosmogenic nuclide. In particular, production rates for neutron reactions (such as ≥20 MeV) are uncertain. Lacking specific neutron cross-section data, proton-induced cross-section data have been used as proxies for neutron cross section. However, for many reactions theoretical considerations indicate that there are large deviations between proton-and neutron-induced cross sections. Aside from a better understanding of the nuclear physics of these processes, applications in geo-and cosmo-chemistry require more precise production rates, which in turn require precise experimentally determined high-energy neutron induced cross-section data. To make these measurements, we used high-energy monoenergetic neutrons produced by the ^{7}Li(p, n)^{7}Be reaction at the Research Center for Nuclear Physics (RCNP), Osaka University. Targets of C, N, O, Mg, Al, Si, K, Ca, Fe, and Ni were irradiated with the neutrons at about 300 and 400 MeV. The long lived nuclides (^{10}Be, ^{26}Al, and ^{36}Cl) were measured by AMS and the short-lived radionuclides (such as ^{7}Be, ^{22}Na, and ^{24}Na) were measured by gamma-ray spectrometry. To investigate the mechanism for nuclear spallation reaction, we also performed neutron irradiations on Cu, Nb, Au and Bi samples and proton irradiations on Cu, Nb and Au samples. In this paper, we will report the experimental procedures for monoenergetic neutron irradiation and compare the cross section data between proton- and neutron-induced reactions.

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EXTRACTION BEHAVIOR OF CARRIER-FREE AND MACRO AMOUNTS OF MOLYBDENUM AND TUNGSTEN FROM HCl SOLUTION

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The aqueous chemistry of molybdenum (Mo) and tungsten (W) is complicated due to the formation of polynuclear species in acid solution. For characterizing chemical properties of element 106, Seaborgium (Sg), therefore, it is quite important to investigate chemical behavior of mononuclear Mo and W species comparable to that of mononuclear Sg complexes; Sg cannot form polynuclear species because of the extremely low production rate in the order of one atom per hour. In this study, solvent extraction experiments of carrier-free and macro amounts of Mo and W from hydrochloric acid (HCl) were carried out to search experimental conditions under which Mo and W form mononuclear species. Aliquat 336 which extracts anionic species from aqueous solution was used as an extractant.

In the experiments with carrier-free Mo and W, ^{90}Mo ($T_{1/2}$ = 5.7 h) and ^{173}W ($T_{1/2}$ = 7.6 min) were produced in the ^{nat}Ge(^{22}Ne,xn) and ^{nat}Gd(^{22}Ne,xn) reactions, respectively, using the RIKEN K70 AVF cyclotron. Reaction products recoiling out of the target were transported to a chemistry laboratory by a He/KCl gas-jet transport system and were deposited on a polyester or Naflon sheet for 5 min. The deposited products were then dissolved in 200 μL of 0.1–11 M HCl. The concentrations of Mo and W isotopes calculated from their radioactivities were approximately 10-13 M. The aqueous phase was mixed with an equal volume of the 0.05 M Aliquat 336-chloroform solution. The mixture was then shaken for 3 min at 25ºC. After centrifuging, 160 μL aliquots of the aqueous and organic phases were taken into separate polypropylene tubes which were subjected to γ-ray spectrometry using Ge detectors. Distribution ratios (D) were obtained from radioactivities of each phase.

In the experiments with macro amounts of Mo and W, $Na_2MoO_4 \cdot 2H_2O$ and $Na_2WO_4 \cdot 2H_2O$ were separately dissolved in 2–11 M HCl. The concentrations of Mo and W were 10^{-3} M and 10^{-5}–10^{-3} M, respectively. Two milliliters of the aqueous phases were mixed with 2 mL of the 0.05 M Aliquat 336-chloroform solution. The mixtures were then shaken for 3 min at 25ºC. After centrifuging, the two phases in each sample were separated for determination of the metal concentrations in each phase. The aqueous phase was evaporated to dryness, and the residue was dissolved in 1 mL of 2 M NaOH solution, while the organic phase was mixed with 2 mL of 2 M NaOH solution to back-extract Mo and W. The metal concentrations in the NaOH solutions were determined spectrophotometrically by a thiocyanate method [1].

The extraction yields of carrier-free Mo and W increase with an increase of HCl concentration ([HCl]) and reach a maximum at around 8 M HCl. The extraction efficiency of Mo is higher than that of W under the studied conditions. The D values of carrier-free Mo and W are in good agreement with those of macro amounts of Mo and W, respectively, in 6–11 M HCl, while the extraction behavior of carrier-free Mo and W is different from that of macro amounts of Mo and W in < 6 M HCl. In higher [HCl], it is reported that the macro amounts of Mo and W exist as monomeric oxochloride complexes such as $MO_2Cl_3^-$(M = Mo and W) [2,3]. Thus, it is found that the carrier-free as well as macro amounts of Mo and W form mononuclear species in 6–11 M HCl. The disagreement in < 6 M HCl would be due to the formation of polynuclear species of the macro amounts of Mo and W. Thus, chemical forms of carrier-free Mo and W cannot be identified at present.

In conclusion, the present extraction system in 6-11 M HCl is applicable to study mononuclear species of Sg compared with those of Mo and W. We will further investigate whether the carrier-free Mo and W exist as mononuclear species in < 6 M HCl.

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IMPROVED NUCLEAR DATA MEASUREMENTS OF ALPHA-EMISSION BRANCHING RATIOS BY ULTRA-HIGH RESOLUTION MICROCALORIMETRY

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The accurate determination of alpha particle-emission branching ratios in certain actinide isotopes is precluded by the lack of energy resolution in modern silicon-based alpha spectrometers. This is because the alpha particle-emission energies of many nuclides are close in energy. This close emission energy, coupled with characteristic low-energy tailing, results in alpha energy spectra that depict overlapping peaks. Further, minor branching ratios often appear as shoulders on the major branching ratio peak. As a result, accurate determinations of close-energy branching ratios are often inferred theoretically or by applying deconvolution routines. As a result, the derived branching ratio values for certain isotopes often have relatively large associated uncertainties. Values of less probable branching ratios are especially susceptible having large uncertainties.

Ultra-high resolution alpha spectrometry may be accomplished by microcalorimetry. These detectors are able to discriminate alpha particle energy with unparalleled precision by measuring the heat deposited by the alpha particle as it interacts with the detector. Detection is facilitated by a superconducting transition edge sensor (TES) that is used to measure the change in temperature of an absorber that is cooled to less than 100 mK. Because incident alpha particles deposit their entire energy within the absorber, there is essentially no dead layer to attenuate particle energy (as in silicon-based detectors). As a result, alpha particle energy resolution of as little as 1.06 keV has been achieved. Therefore, microcalorimeters have great potential to improve upon the determination of branching ratio values for isotopes with close-energy alpha particle-emission energies.

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COMPLETE AND INCOMPLETE FUSION IN ^{9}Be + ^{124}Sn SYSTEM

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Complete and incomplete fusion cross-sections for the ^{9}Be + ^{124}Sn system have been measured around the Coulomb barrier energies (ElabC.B=30 MeV) using the on-line gamma ray detection technique. Two clover detectors were used, one at 125 deg. for absolute fusion cross-section estimation and other at 90 deg (No Doppler shift) for identification of unshifted gamma lines. Along with this two charge particle telescopes and one monitor detector were placed at 65, 160 and 30 deg, respectively. The data have been acquired in the particle-gamma 'OR' condition. The coincidence between 55 deg clover detector and particle telescopes (TAC1, TAC2) was also recorded in ADC. These TAC spectra have been further utilized for putting the gates in the gamma spectra and identification of gamma lines of the residues from incomplete fusion process.

The measured cross-sections have been compared with the one dimensional barrier penetration model and coupled channel calculations. The average angular momentum and the barrier distribution have also been extracted from the measured data and compared with the theoretical calculations.

DEVELOPMENT OF AN ON-LINE ISOTHERMAL GAS CHROMATOGRAPHIC APPARATUS FOR Db AND Sg

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To investigate chemical properties of the transactinide elements dubnium (Db, Z = 105) and Seaborgium (Sg, Z = 106), we have developed an on-line isothermal gas chromatographic apparatus. The on-line experiments with the group-5 and -6 elements using the short lived ^{88}Nb and ^{170}Ta as the homologues of Db and ^{173}W as the one of Sg were conducted. The nuclide ^{173}W was produced in the ^{nat}Er (^{12}C, xn) and ^{nat}Tb(^{19}F, xn) reactions, while ^{88}Nb and ^{170}Ta were produced in the ^{nat}Gd(^{19}F, xn) and ^{nat}Ge(^{19}F, xn) reactions, respectively, at the JAEA tandem accelerator. The apparatus consists of a target chamber, a unit of chemical reaction, an isothermal column made of quartz, and a gas-jet chamber. The target chamber is directly connected to the reaction unit. Nuclear reaction products recoiling out of the target were transported from the target chamber to the reaction unit continuously with He carrier gas. In the chemical reaction unit, the products were stopped on a quartz plug where a reactive gas was introduced. Air saturated with $SOCl_2$ vapor at room temperature was used as the reactive gas. Volatile species produced in the reaction unit were then transported along the isothermal column by the carrier gas flow. Volatile compounds leaving the column were attached to KCl aerosol particles in the gas-jet chamber to transport the products to a detection system. The radioactivity-laden-aerosol was deposited on a glass filter at the collection site of the detection system. An HP-Ge detector was used to measure the γ-rays of each nuclide. In order to obtain the optimum condition for the production of volatile compounds in the online experiments, the chemical yields were measured as functions of the flow rate of the He carrier gas, the flow rate of the reactive gas, and the temperature of the reaction unit. The optimum condition was as follows: 0.75 L/min of the He carrier gas flow rate, 200 mL/min of the reactive gas flow rate, and the reaction unit temperature of 500 °C and 600 °C for Nb and Ta, and for W, respectively. At the above conditions, we measured the relative chemical yields of volatile compounds of ^{88}Nb, ^{170}Ta and ^{173}W as a function of the isothemal temperature. The behavior of W and Nb was the same as that obtained in [1, 2]. It was found that the volatility of compounds of Ta is lower than that of Nb.

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MEASUREMENTS OF ^{10}Be AND ^{26}Al PRODUCTION CROSS SECTIONS FOR Cr, Y AND Tb WITH 285 MeV NEUTRON

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The production cross sections by high energy neutrons are important as basic nuclear data for the estimation of residual radioactivities in the accelerator facility and for deciphering of the cosmic-ray irradiation history by evaluating the amounts of cosmogenic nuclides stored in extraterrestrial matters.
Those cross sections are indispensable to study the formation mechanism of nuclides not only via nuclear spallation and fission reactions but also via fragmentation process by which light nuclides are produced. The formation mechanism of light nuclides via fragmentation process in high energy proton-and photon-induced reactions has been investigated[1, 2]; however, that in neutron has never been reported, except for the high-energy neutron cross section data for C, N, O, Mg, Si, K and Ca presented by Nishiizumi et al.[3] In this work, we tried to measure ^{10}Be and ^{26}Al production cross sections for Cr, Y and Tb induced by neutrons at 285 MeV using accelerator mass spectrometry at Micro Analysis Laboratory, Tandem accelerator, the University of Tokyo, and then to estimate a contribution of fragmentation process from the yield of light nuclides in high energy reactions. The experimental procedure for quasi-monoenergetic neutron irradiation will be reported by Ninomiya et al. in this symposium. Furthermore, we intend to measure ^{10}Be and ^{26}Al production cross sections for Y and Tb induced by protons at 300 MeV and to compare their values with the neutron ones.

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LIFETIME MEASUREMENT OF HIGH SPIN STATES IN 75Br THROUGH DOPPLER SHIFT ATTENUATION METHOD

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High spins states of ^{75}Br nucleus were populated via the ^{50}Cr (^{28}Si, 3p) Br fusion evaporation reaction at an incident beam energy of 90 MeV. The de-exciting γ rays were detected using the Indian National Gamma Array (INGA) [1] consisting of 17 Compton suppressed Clover detectors at Inter University Accelerator Centre (IUAC), New Delhi. We have determined the lifetime of 9 states up to $37/2^+$ for positive parity bands and 12 states up to $37/2^-$ for negative parity bands using the Doppler-shift attenuation method. It is seen that transition quadrupole moments of the positive and negative parity bands remain almost constant before the band crossing and then decrease near the band crossing regions. The decrease in transition quadrupole moments is rather sharp in case of negative parity bands as compared to the positive parity band. Lifetimes from our experiment are 20-30 % less than from previous work done by Luhmann et al. [3]. Experimental results obtained from lifetime measurement are interpreted in the frame work of Cranked-shell model which gives the evidence of shape changes from prolate shape to tri-axial after the band crossing.

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MEASUREMENTS OF THE NEUTRON ACTIVATION CROSS SECTIONS FOR Bi AT 300 AND 400 MEV

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The nuclide-production cross sections by high energy neutrons are important as basic nuclear data for the estimation of residual radioactivities in the accelerator facility and for deciphering of the cosmic-ray irradiation history by evaluating the amounts of cosmogenic nuclides stored in extraterrestrial matters. The nuclide-production cross sections by high energy neutrons can be applied for high energy neutron spectrometry. But the production cross section data for neutron energy are still scarce.

This study aimed to measure the neutron activation cross sections of Bi by using a quasi-monoenergetic neutron field. A quasi-monoenergetic neutrons were produced from a thin Li target (1 cm thick) bombarded by 300 and 400 MeV protons that were provided from the ring-cyclotron of Research Center for Nuclear Physics (RCNP), Osaka University. Since the energy spectrum of this neutron field through the ^{7}Li(p,n) reaction has a high energy peak and a low energy tail, two neutron beams for 0 and 30 degree for proton beam axis were used for sample irradiation to correct the contribution of the low energy neutron components. The neutron energy spectra were measured by using liquid organic scintillator and time-of-flight (TOF) technique.

After irradiation, the gamma-rays from the samples were measured with an HPGe detector. The reaction rates were obtained from gamma-ray spectrum. The neutron activation cross sections were estimated by subtracting the reaction rates of samples for 30 degree irradiation from those of 0 degree irradiation. In this symposium, we will present obtained cross section data with the other experimental data (neutron-induced and proton-induced), and the evaluated nuclear data.

STUDY ON THE SYNTHESIS OF HEAVY ELEMENTS THROUGH NUCLEAR FUSION INDUCED BY OXYGEN-16 ON RARE EARTH TARGETS

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Nuclear fusion of heavy nuclides with heavy ions is of great interest due to its utility for production of the heavy nuclei for the purpose of studies on nuclear reaction and nuclear structure. Especially, fusion of deformed nuclei is getting more attention because of its importance for the discovery for new elements via the hot fusion process of actinide targets. Such fusion process is considered to be characteristic in the threshold of fusion due to the configuration of touching nuclei at the entrance channel. In the present study, barium and lanthanoid targets are used in order to study the effect of deformation in nuclear fusion. The evaporation residues have been measured to obtain the formation cross sections of products and construct the excitation function of fusion and been compared with theoretical calculation.

Targets of barium of natural abundance and rare earths of lanthanum-139, terbium-159 and thulium-169 were prepared in electrodeposition on aluminum foil of high purity up to 99.999% made by Goodfellow. Deformation of relevant target nuclides can be estimated from electric quadrupole moments as +0.245b for Ba-137, +0.2b for La-139, -1.21b for Tm-169 and +1.432b for Tb-159, corresponding to polar radius to equatorial radius in spheroids as 1.01, 1.01, 0.95 and 1.07, respectively, [1] on the assumption of nuclear volumes as $4/3\pi r_0^3 A$ with $r_0 = 1.2$ fm.

Bombardment with oxygen-16 ions was performed at Research Center for Nuclear Physics, Osaka University, Japan. Stacked foil technique and gas jet transport system were applied to measurement of radioactivities of the products by using gamma spectrometry with a Ge semiconductor detector and alpha spectrometry with a silicon surface barrier detector and a PERALS liquid scintillation system. In order to check the incident energy, a Rh target was used for comparison with the reference data, and an Al target with Au catcher foil was irradiated for calibration of the beam current measured with the monitor reaction of $^{27}\text{Al}+^{16}\text{O} \rightarrow {}^{24}\text{Na}$.[2]

Measured nuclides are Gd-149, 147, 146 and Eu-148, 147, 146, 145 for the Ba target, Tb-152m, 152g, 151g, 150m, 150g, 149m, 149g, 148g, 148m, Gd-149, 147, and Eu-146 for La, Ir-182, 181, 180, and Re-177 for the Tm target, and Ta-170, 169, 168, 167 for the Tb target.

The cross sections derived from the radioactivities are compared with theoretical calculations such as the ALICE code [3]. As a result, the threshold of fusion is reproduced well by the calculation for the Tm system while around 5 MeV higher than the calculation for the Ba and La systems. And notable differences between experiment and theory were found for the formation cross sections of several products. The former has some relationship to the deformation of target and the latter is related to the deexcitation process of the fused nuclei. We are still in constructing accurate excitation functions for the relevant nuclear systems in order to make the progress to discussion of the effect of deformation.

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PO-2-9-1 22310

AN ANALYTICAL FIGURE OF MERIT (AFOM) FACTOR FOR EVALUATING ADVANTAGES OF ANTICOINCIDENCE GAMMA-RAY SPECTROMETRY IN NEUTRON ACTIVATION ANALYSIS

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One of the most important advantages of anticoincidence gamma-ray spectrometry for trace element analysis is the substantial decrease of background activity. A disadvantage, however, is the reduction of peak area efficiency if the gamma-ray involves cascade decay modes. A few attempts have been made to derive a general equation for assessing the advantages of using anticoincidence counting for different nuclides and sample matrices. But many of these approaches appear not to be practical for real samples. Others consider the improvement in peak-to-background ratio only and do not take into account the improvement of counting statistics in the net peak area. The influence of sample matrix is not considered in another case. We have attempted to define an analytical figure of merit factor (AFOM) for assessing the advantages of anticoincidence counting which would satisfy the following requirements. The AFOM should (i) take into account most of the parameters related to sensitivity of a peak, such as resolution, peak area, background around the peak, dead time, counting time, and counting statistics; (ii) be general and should represent changes in the sample matrix composition; and (iii) provide parameters that can be easily measured. In order to demonstrate the effectiveness of the AFOM term developed in this work, 15 biological reference materials (RM) and standard reference materials (SRM) supplied by NIST and one RM by IAEA containing diverse ratios of Mg to Mn were analyzed for Mg by INAA using the 1014.4 keV gamma-ray of ^{27}Mg.

PO-2-9-2 21468

SELECTED TRACE AND MINOR ELEMENTS OF BOTTOM SEDIMENTS FROM ACARAY RESERVOIR

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Comision Nacional de Energia Atomica

Minor and trace elements from bottom sediments of Acaray Dam reservoir were investigated with XRF techniques. The lake covers an area of 20 km^2 and a volume of 100x10^6 m^3. It was built on the Acaray River, in the Alto Paraná region of Eastern Paraguay.

Trace elements analyzed were the refractories Y-Rb-Sr-Zr-Nb-Ba-La-Ce-Nd, using and Am source and minor elements Ti-Mn-Fe- with a Cd source. Sediments play an important role in the distribution of trace elements in the aquatic system and act as a sink for metals. REE are considered useful geoindicators. Samples were taken from 6 different sampling stations. It was found good correlations with sediments from Itaipú Dam segmented body and at some sampling sites Ce positive anomaly.

PO-2-9-3 20919

QUANTITATIVE TRAIT LOCUS ANALYSIS FOR SEED ZINC ACCUMULATION IN MODEL LEGUME, LOTUS JAPONICUS

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Phytoremediation is a promising method for purifying the soils polluted with heavy metals. This environmental restoration technology utilizes plant activities for the absorption and removal of heavy metals from the contaminated soil. Among the highly-diverse plant species, several plants which accumulate remarkably high concentration of heavy metals were identified. But these "hyperaccumulators" are very small and the total amounts of heavy metals removed from the contaminated soils are not so large. Therefore, an ideal plant for the phytoremediation should have not only an ability to accumulate heavy metals but also a large biomass. Based on these requirements, we focused on the seed zinc accumulation mechanisms in *Lotus japonicus*. *Lotus japonicus* has been proposed as a model legume for molecular biology, and the results obtained from *Lotus japonicus* are applicable to the large biomass crop, soybean. From our previous work, zinc accumulation pattern was different between two *Lotus japonicus* cultivars Gifu B-129 and Miyakojima MG-20, therefore, an objective of this study was to use a *Lotus japonicus* recombinant inbred population (Gifu B-129 × Miyakojima MG-20) to determine the loci governing seed zinc concentrations and to use these loci to propose candidate genes whose expression might contribute to these characteristics.

The seeds of forty-five lines which were grown for seed harvest at the same condition were obtained from the *Lotus japonicus* National BioResource Project in Japan and the measurement of seed Zn concentration were performed. In this study, neutron activation analysis was applied to measure zinc concentration in seeds. The seed samples were sealed in a polyethylene vinyl bag and were irradiated for 17 minutes in the research reactor, JRR-3M installed at the Japan Atomic Energy Agency, with a thermal neutron flux of $5.2 \times 1013\ \mathrm{n{\cdot}cm^{-2}{\cdot}sec^{-1}}$. After irradiation, gamma-rays emitted from the sample was measured by a Ge(Li) detector. The gamma-rays used to determine ^{65}Zn was 1.116 MeV.

In the previous work using ^{65}Zn as a radio active tracer, seed ^{65}Zn accumulation was higher in Miyakojima MG-20 than Gifu B-129 after 48 hours ^{65}Zn uptake period. However, in the present study, the concentration of Zn in seed was 1.6-fold higher in Gifu B-129. This contradiction might be reflected the difference of seed maturation process and period between two cultivars. Gifu B-129 needs longer period for seed maturation than Miyakojima MG-20. These results suggested that the comparison of Zn accumulation in the whole seed maturation period will provide the index for the Zn storage mechanisms in the seed. From these view points, J/qtl program was used to identify QTL related to the Zn storage in seed. Using marker regression method, J/qtl identified one major QTL at chromosome 2. The genes localized in this QTL were investigated based on the *Lotus japonicus* genome sequence and several Zn accumulation related genes and one seed maturation related gene were found. The relationship between these genes and Zn accumulation in seed will be discussed.

PO-2-9-4 20412

CHARACTERISTICS OF THE TRACE ELEMENTS IN INDOOR PM10 AND PM2.5 AT SUBWAY STATION USING NEUTRON ACTIVATION ANALYSIS

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Airborne particulate matters, especially the PM2.5 (aerodynamic equivalent diameter, AED, less than 2.5 μm) fraction has been important. This is because of their potential for deposition on to the human respiratory system being accompanied by many harmful trace metals (such as As, Cd, Cr, Cu, Mn, Pb, Se, and Zn) [1]. The indoor air quality has become a great concern since late 1980s, because the population spends a majority of their time in various indoor environments [2]. The indoor particulate matter may be influenced from outdoor environment and indoor sources such as combustion devices, cooking, etc. In this study, a total 60 of PM10 and PM2.5 samples was collected on spring and summer season in 2009 with low volume air sampler at one subway station in Daejeon, Korea. We undertake the measurements of about 26 elements in PM10 and PM2.5 using instrumental neutron activation analysis (INAA). Based on our measurement data, we characterize elemental concentration status and mutual relationship between PM10 and PM2.5. The average concentrations of PM10 and PM2.5 were 66.6 ± 15.8 $\mu g/m^3$ and 42.5 ± 10.4 $\mu g/m^3$, respectively. The highest daily mass concentrations of PM10 and PM 2.5 were 97.5 $\mu g/m^3$ and 72.7 $\mu g/m^3$, respectively, at same day (5 May, 2009) in spring season. The average PM2.5/PM10 indicates that about 65% of the PM10 was made up of PM2.5. The correlation coefficient between PM2.5 and PM10 was 0.651. For the INAA determination of Al, As, Ba, Br, Ce, Co, Cl, Cr, Cu, Cs, Fe, I, In, K, La, Mg, Mn, Na, Sb, Sc, Sm, Se, Th, Ti, V, and Zn, the PM10 and PM2.5 samples were irradiated using thermal neutrons using the Pneumatic Transfer System (PTS, Φth = 2.95 x 10^{13} $cm^{-2}s^{-1}$, Rcd= 250) at the HANARO research reactor at the Korea Atomic Energy Research Institute. The measurements were carried out using a high-purity Ge detector with a relative efficiency of 25%. Mutual relationship and characteristics of elemental concentrations in PM10 and PM2.5 are compared and discussed.

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OPTIMIZATION OF PERFORMANCE OF A CHANNEL MODERATOR OF A PGNAA SETUP FOR CARBON, NITROGEN, AND OXYGEN DETECTION

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The Prompt Gamma Neutron Activation Analysis Technique (PGNAA) has proven to be an efficient technique to determine concentration of C, O, H and N elements in low Z elements bulk samples for the detection of contraband. The elemental ratio C/O in low Z samples is used to distinguish between contraband and innocuous materials. The elements C N, and O are detected in neutron inelastic scattering (NIS) reactions using 6.0-14 MeV neutrons while Thermal Neutrons are used to detect H through Thermal Neutron Capture gamma rays. Therefore, an efficient detection of H, C, N and O in PGNAA setup requires a moderator geometry that produces a maximum fast/slow neutron flux ratio. A polyethylene moderator can be used in conjunction with 14 MeV neutron source to produce such mixed flux. Previously polyethylene moderators have been used successfully at King Fahd University to produce thermal neutrons flux using 2.8 MeV neutrons from D(d,n) reactions . In this study Monte Carlo simulations were carried out to optimize the design of a high density Polyethylene moderator to produce the desired mixed flux of fast and thermal neutrons at the sample location using a 14 MeV neutron source. In order to optimize the fast/slow neutron yield, channels with varying diameters and inclination angles were drilled through the moderator thereby providing paths of variable attenuation to the 14 MeV neutrons. The effect of the number, size, and inclination angles of the channels on the fast/slow yield ratio was studied. The results of these studies will be discussed.

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PRELIMINARY RESEARCH FOR IRIDIUM IN CRETACEOUS-TERTIARY BOUNDARY CLAY USING MULTI GAMMA RAY DETECTION

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The Cretaceous-Tertiary (K-T) boundary about 65 million years ago records a mass extinction event caused by a bolide impact. In order to clarify the type of the bolide, K-T boundary clay collected from Stevns Klint, Denmark was preliminarily investigated in this work [1]. The specimens were removed from a thin layer of marl, which is known as fish clay. Iridium concentrations of fish clays across the K-T boundary were determined using a multiple gamma-ray analysis system after neutron activation. The iridium in the geological samples was determined using the multi-parameter coincidence method with no chemical separation after neutron irradiation. Fifty to one hundred mg of ground homogenized fish clay sediment samples were sealed in pure quartz vials and then irradiated for 48 hours in the JRR-3 reactor at JAEA with a neutron flux of 9.6×10^{13} $\mathrm{ncm^{-2}s^{-1}}$. 100 ng standard iridium samples made from diluted Ir standard solution (ACROS Organic Co.) were also prepared, sealed in quartz vials, and then irradiated together with the sediment samples. After irradiation, the samples were cooled for about four weeks. The gamma ray decay was measured using GEMINI-II, an array of 16 high purity Ge detectors, with a typical measurement taking about a day. The γ–γ coincidence peak of 468-316 keV from ^{192}Ir ($T_{1/2}$ = 73.8 d) produced by the ^{191}Ir(n,γ) 192Ir reaction was used in quantitative analysis. All the samples were measured with a standard ^{133}Ba source to perform dead-time calibration of the detector system. The iridium content of the sediment samples was obtained by comparing the ^{192}Ir intensity of the sediment samples with the standard iridium after decay time corrections. In the analysis, anomalously high Ir concentrations were detected in some marl samples, with the highest concentration being about 30 ppb.

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APPLICATION OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS FOR EXAMINATION OF OIL PIGMENTS

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The aim of this work was to identify the applicability of instrumental neutron activation analysis as a non-destructive examination tool for the quantitative composition analysis associated with authentication, restoration and conservation of art objects in the field of cultural heritage. The analysis of oil pigments was carried out using NAA and PGAA facilities of the HANARO research reactor at the Korea Atomic Energy Research Institute in collaboration with the National Museum of Contemporary Art in Korea. It was possible to accumulate a number of quantitative data on the concentrations of major, minor and trace elements in white, black, red yellow colors of Rambrant oil pigments recently collected at the Korean market. Analytical quality control was implemented using NIST SRM, certified reference materials and standards. The concentrations of major elements such as Al, Ca, Cr, Cu, Fe, S, Ti and Zn were compared with those of XRF method. Thus, the analytical results for 30 trace elements will be useful to identify the application and the possibility of the characteristics of pigment sources, similarity degree of constituents, presumption and classification of place, period and processes of a production according to the origin of materials. The statistical treatments such as correlation and pattern analysis, principal components analysis, bivariate cluster and discriminant analysis were applied to the data set measured.

DETERMNIATION OF DEGRADATION CONSTANT OF Li ION FROM ^{10}B(n,αγ)^{7}Li REACTION IN VARIOUS MEDIA

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A Li ion in a medium undergoes a large degradation due to its high stopping power. This phenomenon in a ^{10}B(n,αγ)^{7}Li reaction induced by a thermal neutron influences a peak line shape of gamma-rays. 477.6 keV gamma line emitted from an excited 7Li nucleus recoiled by an energetic alpha particle is broadened and its peak line shape in a spectrum varies according to the slowing-down media. A numerical study for the analysis of the line shape has been conducted by performing a parametric search and fitting the measured spectrum in a least squares approach by Choi et al [1] and implemented in a recent version of HYPERGAM code.

The gamma-ray spectra were measured for various media like an elemental boron, a boric acid, a borax, a boron carbide, a boron steel and so on at a SNU-KAERI prompt gamma activation analysis facility of the HANARO research reactor in Korea Atomic Energy Research Institute. The degradation constant was determined as between 1.2 ~ 2.5 ps^{-1} according to the slowing-down media.

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HYBRID NEUTRON ACTIVATION ANALYSIS FOR STUDY OF ORGANIC HALOGENS IN PRECIPITATION IN BEIJING, CHINA

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Due to their severe carcinogenicity, mutagenicity and teratogenicity, as well as persistence and bioaccumulation, organic halogens have gained utmost attention all over the world. In particular, wet deposition has been monitored, as dry deposition only contributes to a minor extent of the total deposition of PCBs and OCPs. In this study, the concentrations of extractable organic halogens (EOX), persistent extractable organic halogens (EPOX), PCBs and OCPs were measured by a hybrid NAA method combined with GC-MS in precipitation samples collected from Beijing, China, from May 2006 to June 2008. The corresponding analytical quality control measures were taken during the whole experiment. The concentrations of EOI, EOBr and EOCl in all the samples were 0.13~2.06 μg/L, 0.11~1.99 μg/L, 9.93~262.73 μg/L, respectively ; 0.03~0.95μg/L, 0.02~0.53μg/L and 4.61~110.67μg/L for EPOI, EPOBr and EPOCl, respectively. EPOX/EOX ranged from 24 % to 44 %, which indicated the major EOX in precipitation were acid-liable or acid-soluble. The relative proportions of the known organochlorines (84 PCB congeners + 10 OCPs) to total EPOCl were very low (< 1.5 %). Significant correlations between the concentrations of EPOCl and EPOBr or EPOI, and EOCl and EOBr or EOI were observed, which suggested that those contaminants in precipitation might mainly come from the same sources. There were no clear seasonal trends for the concentrations of EOX and EPOX. The highest concentrations of organic halogens in snow demonstrated that the scavenging ability of organic halogens by snow was higher than rainwater. The range of monthly fluxes of ΣHCHs, ΣDDTs and ΣPCBs were 37~841 ng·m^{-2}·month^{-1}, 0~1739 ng·m^{-2}·month^{-1} and 0.71~75.62 μg·m^{-2}·month^{-1}, respectively. Fluxes of PCBs and DDTs decreased with time, which showed that the consumption of those contaminants have significantly decreased or not been used in recent years, which fully demonstrated that the ban on the use of DDTs and PCBs in China was very effective.

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EVALUATION OF SYNTHETIC CONDITIONS OF ZIRCONIUM MOLYBDATE GEL FOR USE IN THE ^{99}Mo/^{99m}Tc GENERATORS

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Zirconium molybdate gel has excellent characteristics for use as column matrix material of generators. The preparation conditions of zirconium molybdate gel directly influence its chemical and physical properties and thus the generator performances. This work describes the effect of several parameters of zirconium molybdate gel synthesis on the ^{99}Mo/^{99m}Tc generator performance. The physicochemical properties of the gels as well as their behavior as technetium-99m generators have been evaluated to prepare gels with consistent properties.

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PRODUCTION OF RARE EARTH MULTITRACER FROM natHf WITH 135-MEV/NUCL. 14N IONS

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Physical and chemical properties of rare earth elements (REEs) bear a strong resemblance to each other, and thus it is interesting to investigate how each REE differently distributes in the same experimental system. A multitracer including many radionuclides of REEs, which enables efficient and simultaneous tracing of a number of REEs under an identical experimental condition, is very useful for the above purpose [1,2]. Thus far, the REE multitracer produced from a ^{197}Au target irradiated with a 135-MeV/nucl. ^{14}N beam from the K540 RIKEN Ring Cyclotron (RRC) has been used by many researchers in the fields of chemistry, biology, geology, and environmental sciences [3,4]. In these experiments, the multitracer was prepared by removing the Au material through a solvent extraction with ethyl acetate, so that γ peaks of REEs were often below detection limits due to those of many other elements formed from ^{197}Au. In this paper, we propose a novel method to produce the REE multitracer using ^{nat}Hf as a target. The metallic Hf target is stable for high-intensity heavy-ion bombardments, and production yields of rare earth radionuclides from ^{nat}Hf are expected to be larger than those from ^{197}Au.

The REE multitracer was produced from the ^{nat}Hf foil (99.9% in purity and 165 mg/cm^2 in thickness) irradiated with the 135 MeV/nucl. ^{14}N beam from RRC. A ^{197}Au foil (465 mg/cm^2 in thickness) and a ^{nat}Cu beam monitor (43 mg/cm^2 in thickness) were also mounted in the same target stack. The ^{14}N beam intensity was about 0.6 particle μA. For effective productions of short- and long-lived radionuclides, two separate target stacks were irradiated for 30 min and 59 h, respectively. After the irradiations, REEs were chemically separated from the ^{nat}Hf target according to the procedure shown in Fig. 1. For a comparison with the previous method with the ^{197}Au target, REEs were also separated from Au using the similar anion- and cation-exchange procedures shown in Fig. 1. The REE multitracers were then subjected to γ-ray spectrometry using a Ge detector. As a preliminary result, about 20 radionuclides of Y, Ce, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were identified in the short irradiation of ^{nat}Hf. Chemical yields of over 80% were obtained for those nuclides. A separation factor for the Hf target material was evaluated to be 3×10^{-3} based on the 343-keV γ peak of ^{175}Hf. In the conference, the results on the long irradiation will be also presented by comparing with the ^{197}Au results.

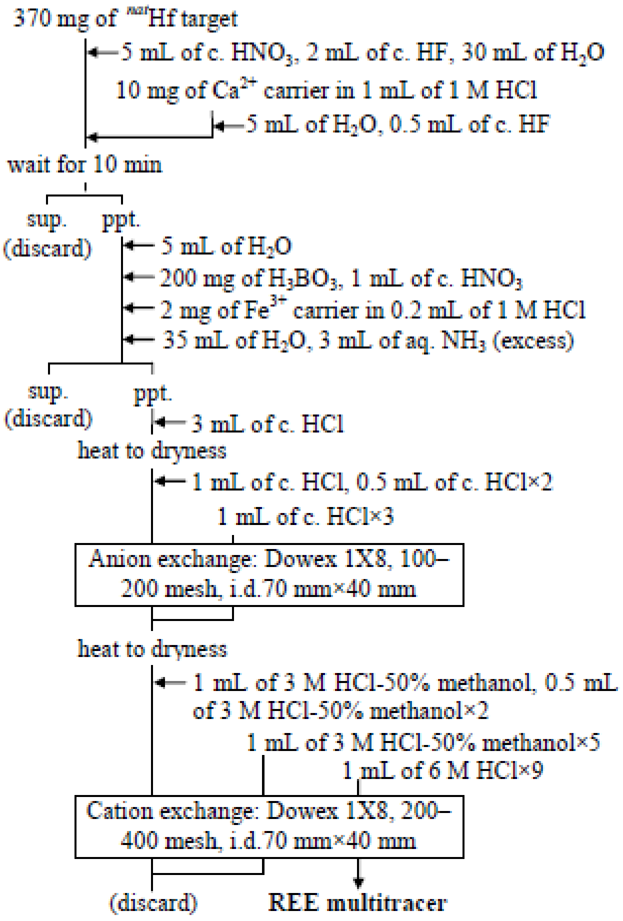

Fig. 1. Schematic diagram for separation of the REE multitracer from a ^{nat}Hf target.

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EVALUATION OF SCANDIUM-POLYAMINOPOLYCARBOXYLIC COMPLEXES AS A NEW GENERATION OF PET AGAENT AND RADIOPHARMACEUTICAL

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Scandium isotopes (^{44}Sc and ^{47}Sc) are becoming more available due to development of generators. Their properties are convenient for both PET imaging or for radiotherapy. To use them in nuclear medicine, ligands forming complexes endowed with a high stability are necessary. However, complexation chemistry of trivalent scandium has not been studies well enough to suggest suitable ligands. Ligands of the polydentate aminopolycarboxylates such as DTPA, DOTA, NOTA or TETA, are initial choices since they form stable complexes with lanthanide(III) ions and with Y(III) belonging to the same column as Sc(III) of the periodic table. The determination of the thermodynamic stability constants of these ligands with Sc(III) is needed to determine which ligand is optimal.

Available experimental data on stability constants of complexones such as DTPA, DOTA, NOTA and TETA have been published for some time and are recognized as reference values. Scandium is the exception since no relevant data is available. For the first time, reasonable numerical values of stability constants of Sc(III) with H3NOTA, H4TETA, H4DOTA and H5DTPA were obtained by potentiometry, ^{1}H/^{45}Sc NMR and a displacement method.

The aim of this work is i) to determine the number and stoichiometry of the complexed species and ii) to report the stability constant values for Sc^{3+} with DOTA, DTPA, NOTA and TETA using potentiometry together with ^{1}H/^{45}Sc NMR measurements. In addition, a radiochemical displacement method was employed to determine the stability constants at the tracer level, using a cationic exchange resin. Finally, it is of benefit to screen metal complexes of radiopharmaceutical interest in vitro, to gauge qualitatively their potential in vivo stability and hence their suitability for further biological studies. In this work we also describe a series of in vitro assays to asses the potential in vivo stability of these potentially new radiopharmaceuticals.

SYNTHESIS AND EVALUATION OF ^{76}Br LABELED GLUCOSE FOR TUMOR DIAGNOSIS WITH PET

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Objectives: ^{18}F-FDG is most valuable tool for tumor diagnosis with PET, but ^{18}F is limited to use for its short half-life, 110 minutes. Usually, radiopharmaceuticals with little long half-life are convenient to use. ^{76}Br is a radioactive halogen such as ^{18}F or ^{123}I, and has appropriate half-life (16.1 hour). It is suitable for labeling of various compounds developed for labeling with ^{18}F or ^{123}I. So we hoped to develop radiopharmaceuticals labeled with ^{76}Br for tumor diagnosis with PET. For this purpose, glucose derivatives like ^{18}F-FDG are attractive candidates. Various glucose derivatives labeled with ^{123}I or ^{99m}Tc were developed, but none of them have shown an effective property for tumor diagnosis. In this study, we synthesized ^{76}Br labeled glucose (^{76}BrDG) and evaluated its utility for tumor diagnosis.
Methods: ^{76}Br was produced via the ^{76}Se(p,n)^{76}Br reaction by irradiating $Cu_2{}^{76}Se$ pellet with 20 MeV proton. ^{76}BrDG was synthesized from mannose triflate with almost the same method of ^{18}F-FDG. We prepared LL/2 tumor bearing mice and administered ^{76}BrDG and ^{18}F-FDG. The biodistribution of them were determined at the designated times after injection. PET studies were performed on the mice bearing LL/2 tumor with microPET.
Results: The radioactivity of ^{76}Br was 250 MBq (EOB) for 8 hours irradiation. The overall synthesis time of ^{76}BrDG was 60 min and the radiochemical yield was about 50%. The biodistribution studies showed that ^{76}BrDG accumulated to tumor with the almost same degree of ^{18}F-FDG. PET imaging studies of ^{76}BrDG demonstrated clear images of tumor, which is similar with that of ^{18}F-FDG.
Conclusion: In this study, ^{76}BrDG was highly accumulated to tumor and it has been great potential for tumor diagnosis. We will examine the uptake to various tumors with ^{76}BrDG in future.

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SYNTHESIS OF 77Br LABELED PHENYLALANINE: A PRELIMINARILY INVESTIGATION FOR THE PREPARATION OF RADIOBROMINE LABELED PEPTIDES

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Introduction: Bromine-76 $^{(76\mathrm{Br}}$, $t_{1/2}$= 16.1 h, β^+ = 57%) can be applicable for in vivo imaging with positron emission tomography (PET), and has great potentials for clinical applications. We have produced no-carrier-added ^{76}Br by using AVF cyclotron in JAEA, and have exploited ^{76}Br-labeled radiopharmaceuticals. Since biologically active peptides have high affinity for receptors, many radiolabeled bioactive peptides have been employed for clinical and preclinical investigation in nuclear medicine. Thus, it is expected that ^{76}Br labeled peptides are also promising for in vivo imaging of various diseases with PET. In this study, as a preliminarily investigation to exploit ^{76}Br-labeled peptides, [^{77}Br]-N-Boc-(p-bromo)-L-phenylalanine methyl ester, a building block of peptides, was synthesized by using ^{77}Br ($t_{1/2}$ = 57.0 h, EC = 99%) which has suitable half-life to assess the chemical properties of radiobromide compounds.

Methods: No-carrier-added ^{77}Br was produced by the ^{nat}Se(p,xn)^{77}Br reaction using a $Cu_2{}^{nat}Se$ target. Irradiation was performed for 7.5 h using proton beams of 20 MeV at a beam intensity of 5 μA. ^{77}Br was separated by the dry distillation method[1] . N-Boc-p-(tri-n-butylstannyl)-L-phenylalanine methyl ester, a precursor of radiobromide amino acid, was synthesized from N-Boc-p-iodo-L-phenylalanine methyl ester and bis(tri-n-butyltin) in the presence of Pd(0) catalyst[2] . Labeling experiments were performed at r.t. for 30 min. by using 37 kBq of ^{77}Br and 100 μg of precursor in the presence of 100 μg of chloraminT (CAT). Labeling efficiency was determined by TLC analysis (dichloromethane: hexane = 10:1). Characterization was also performed TLC and HPLC analysis.

Results: 70 MBq of no-carrier-added ^{77}Br was obtained at the end of bombardment. No other radionuclide was contained in the separated ^{77}Br. We have successfully synthesized [^{77}Br]-N-Boc-(p-bromo)-L-phenylalanine methyl ester with high labeling efficiency (more than 70%) in the presence of 100 μg of CAT. Now we optimize the labeling condition such as concentration of precursor, oxidizing reagent, and reaction temperature. We will discuss the labeling efficiency under various conditions, and the possibility to prepare ^{76}Br-labeled peptides which can be applicable for in vivo imaging with PET in nuclear medicine.

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A XANES STUDY OF ANCIENT THAI GLASS

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Glasses have been used as ornaments and decorations in Thailand for several hundred years. In this work, the blue-coloured ancient decorative glasses from archaeological findings as well as fragments of artifacts were identified for the first time by means of a synchrotron-based technique called: X-ray absorption near edge spectroscopy (XANES). Results indicated that they were lead-bearing glass. The presence of copper has attributed mainly to the various shade of blue colouration. The XANES is a powerful yet non-destructive technique for archaeological studies of such ancient glassy materials.

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AIR POLLUTION IN CHEMICAL ELEMENTS, DETERMINED BY INAA, AND CHILDHOOD LEUKAEMIA IN PORTUGAL

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Previous studies on the association between air pollution and childhood leukemia focused mainly on air pollution from traffic but did not consider the effects of individual elements. In recent decades, a number of techniques have been developed to monitor concentrations of elements in the air. Biomonitoring is one of such techniques. It uses bio-organisms (biomonitors), such as mosses and lichens, to obtain quantitative information on certain characteristics of the biosphere. Lichens can be effectively used as biomonitors because they depend largely on atmospheric depositions for their nutrient supply, thus showing elemental compositions which reflect the gaseous, dissolved and/or particulate elements in the atmosphere. This study aims to investigate whether elemental chemical elements in atmospheric deposition obtained via lichen biomonitoring might be associated with child mortality due to leukemia in the Portuguese population. A former publication pointed out a non-significant positive association between the risk of childhood leukemia and levels of arsenic, mercury and lead, and a non-significant negative association between the disease and the level of nickel. Lead seems to show a weaker association with childhood leukemia than arsenic and mercury. A Bayesian hierarchical model was used to explore the association between lichen biomonitoring measurements of elements and childhood leukemia death counts taken at small administrative units. We aim to apply similar spatial regression analysis to the whole dataset, obtained by Instrumental Neutron Activation Analysis (INAA) and Prompt Induced X-Ray Emission (PIXE), attempting to find any significant association between the disease and any chemical element.

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The opinions presented are those of the author and not necessarily those of the United Nations.

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ANALYSIS OF AIR PARTICULATE MATTER IN TEFLON™ AND QUARTZ FILTERS BY SHORT-IRRADIATION, EPITHERMAL-NEUTRON ACTIVATION WITH COMPTON SUPPRESSION

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A fast methodology combining epithermal neutron activation analysis (ENAA) with Compton suppression, and featuring short irradiation, short decay and short measurement times, has been applied to the characterization of airborne particulates collected in Teflon™ and quartz filters, respectively at an inner-city location in an urban environment (Lisboa, mainland Portugal), and at a remote, rural location in an oceanic environment (Terceira island, Azores). Fluorine and silica are the main components of Teflon™ and quartz filters, respectively; the latter also have higher contents of residual elements in their blanks. Mass concentrations (PM2.5) were 5-96 $\mu g \cdot m^{-3}$ in Teflon™ filters and 5-86 $\mu g \cdot m^{-3}$ in quartz filters, thus within the same order of magnitude. The analyzed filter areas were similar as well. All samples were irradiated in the rapid pneumatic transfer system (SIPRA) implemented at the Portuguese Research Reactor of the Technological and Nuclear Institute (RPI-ITN), inside cadmium foils (thermal/epithermal neutron ratio ≅2). Gold monitors were irradiated every 10 samples, to check upon the neutron-flux variation. Two reference materials – NIST SRM® 1633a 'Trace Elements in Coal Fly Ash' and NIST SRM® 1648 'Urban Particulate Matter' (~20 mg each replicate) – were irradiated immediately after the monitors and before the samples. Measurements were carried out under Compton-suppression conditions: five ORTEC® crystals all around and one on top, with detector and electronics from CANBERRA®. Epithermal short irradiation associated to this suppression system enabled the determination of elemental tracers that can be ascribed to major emission sources: sea spray (Cl, Na, Br, Mg), oil burning (V), waste incineration (Cl), soil resuspension (Mg, Mn, Na, U, V), and vehicular traffic (Br, Mn). In a few cases, the same element likely has different origins for the mainland and island collections. Accounting for method uncertainties, the accuracy of the determinations may be viewed as good.

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CHARACTERISATION OF BIOMONITORS USED IN METAL AIR POLLUTION STUDIES: CAPACITY, pK-VALUES AND METAL-EXCHANGE BEHAVIOUR OF Parmelia sulcata

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Despite the knowledge of lichens for environmental monitoring studies, the chemical properties and mechanisms governing metal uptake and sequestration by these organisms remain unclear. To address this problem a series of experiments were done with *Parmelia sulcata* Taylor collected in Portugal from the *Olea europea*. Each of a few samples was immersed in milli-Q water using three different (water volume/lichen mass, V/m) ratios: 50, 100 and 200. Titration data were modeled using a least squares fit. Two models were analyzed: 1) assuming the lichen to be a 2 protic (organic) acid, 2) assuming the lichen to be a 3 protic (organic) acid. Since the acid (lichen) concentration and the total amount of proton initially present are not known, they were treated as fitted parameters along with the dissociation constants (pK's). The model assuming 3 proton sites was accepted after comparing the sum of squared deviations using an F-test. Metal uptake capacity or proton-metal exchange behavior was measured by titration of the lichen (V/m=50) with respectively $CaCl_2$, $NiCl_2$ and $MgCl_2$. Titration data were modeled using a least squares fit in Excel. Acid dissociation constants were fixed to the values previously found for volume/mass ratio 50. The acid (lichen) concentration and the total amount of proton present (not initially) were again treated as fitted parameters along with the dissociation constant (pK-ML). For comparison, the pH change after adding the metal was calculated.

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CHARACTERISATION OF SOILS, PLANTS AND WATER SAMPLES COLLECTED AT SÃO DOMINGOS MINE, PORTUGAL

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This study has been designed to select an optimal bioaccumulator of arsenic among the native plants growing around the former copper-mining complex of S. Domingos, Portugal. The complex is located at the Lower Alentejo area of southern Portugal, in the heart of the Iberian pyrite belt. The mine site is thought to have been excavated since the Chalcolithic Age, and continuously --and most intensively -- from 1855 through 1966, when the whole operation was shut down for depletion of the ore reserves. The mine has never been properly decommissioned, and its effective abandon has caused a serious impact in local ecosystems, regional watershed and the environment at large. For bioaccumulator selection, a few vascular plants were collected at six locations around the derelict mine, together with soil and runoff-water samples. Back in the laboratory, each plant was split into roots, stems, leaves and flowers (when available). All parts were washed with distilled water, freeze-dried, ground to a powder in a nitrogen-cooled, Teflon mill, and replicates (~200 mg) were then weighed and neutron-irradiated. Soil samples were sieved through a 1-mm nylon mesh, weighed (~100 mg) and irradiated. Lyophilized water samples were also irradiated within polyethylene canisters. Arsenic and other chemical elements were determined through gamma-ray spectra taken 2 and 28 days after irradiations. Generally speaking, values in plant components may vary by two orders of magnitude. Transfer coefficients for the chemical elements --that is ratios between the element in plant components and the substrata where those plants had grown, either water or soil --are discussed in terms of relative apportionment and overall indication, and in view of the potential arsenic inputs from the ground media.

APPLICATION OF NAA TO THE TRACE ELEMENTAL DETERMINATION FOR NAIL SAMPLES FROM RESIDENTS OF TOKYO, JAPAN

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Introduction Instrumental neutron activation analysis (INAA) was selected for the analysis of fingernail samples because of its almost contamination-free sample preparation and multi-element analysis capability. As there are few published data of trace elements in fingernails of residents of Tokyo and even of Japanese, we aim to present the trace element concentration data for fingernails of healthy individuals residing in suburban area of Tokyo. The data obtained are then discussed in terms of gender and living habits among the participants. In addition, the present results are compared with data from literatures reporting elemental concentrations in nail samples.

Experimental Fingernail samples (from 10 fingers) were collected from a total of 18 individuals (11 males, 7 females) with an average age of 27.7 years old. The samples were washed with acetone and deionized water. About 10-40 mg of fingernail was double-sealed in acid-cleaned polyethylene bags. The nail samples along with NIST 1566b (Oyster Tissue) for quantification and NIES No. 5 (Human Hair) and NIST 1577a (Bovine Liver) for quality control were simultaneously irradiated with reactor neutrons at the Japan Atomic Energy Agency.

Results and discussion With changing irradiation and cooling times, 18 elements (Ag, Al, As, Ca, Cl, Co, Cu, Fe, Hg, K, Mg, Mn, Na, S, Sb, Se, V, and Zn) could be reliably determined. The results showed that the toxic elements in the fingernails of this study are in the lower range among literature values. No chronic exposures to toxic elements such as As and Hg were found. The level of Hg found is lower than that reported 20 years ago, highly possibly due to the strict regulation control in Japan on the release of Hg to the environment. The element contents of Se and Zn in nails are not variable among participants and are in agreement with results from other countries. In critically scrutinizing of the data of this study as well as those reported in literatures, we found not a few values are doubtful in the literatures. With excluding such values, the overall data of this study showed similar concentrations to those of healthy participants from other countries. The current data could represent the background level of elemental concentrations in fingernails of residents in Tokyo and serve as reference values for future study.

DETERMINATION OF ULTRA-TRACE RARE EARTH ELEMENTS IN UREILITE METEORITES BY RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS WITH AN EMPHASIS OF THE CORRECTION FOR THE CONTRIBUTION CAUSED BY NEUTRON INDUCED FISSION OF URANIUM

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Rare earth elements (REEs) are a group of elements whose abundances contribute the most significantly in geochemistry and cosmochemistry. While REEs are generally abundant in terrestrial samples, they are depleted in most meteorite samples and are highly depleted in a few types of meteorites. Ureilites are among them. REE abundances in ureilites are too low to be reliably determined by ICP-MS and can be accurately determined only by radiochemical neutron activation analysis (RNAA). In this study, we aimed to determine REEs in several ureilites by RNAA. To obtain accurate data of REEs, the contribution of neutron-induced fission reaction of ^{235}U to light REEs (LREEs) was seriously considered and aimed to be properly collected. Ureilite meteorites as well as two control samples (Allende meteorite and a peridotite geostandard samples JP-1) were analyzed in this study. About 70 mg powder of each sample was sealed in a quartz vial and irradiated with neutrons along with REE chemical standards in the JRR-3 reactor of Japan Atomic Energy Institute. The RNAA procedure was mostly based on Minowa and Ebihara (2003) [1], consisting of twice column separations and precipitations of hydroxide and fluoride. Chemical yields were obtained by using inductively coupled plasma atomic emission spectrometry (ICP-AES). Ten REEs (La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb and Lu) were able to be determined. CI Chondrite-normalized REE abundances for ureilites show either so-called V-shaped pattern or LREE-depleted pattern. A LREE-depleted pattern is probably resulted from the absence of plagioclase component while a V-shaped pattern represents either the contamination of LREE-enriched terrestrial component or the presence of trapped liquid component produced during igneous process on ureilites parent body (ies). As ^{140}La, ^{141}Ce and ^{147}Nd are produced by neutron-induced fission reaction on ^{235}U (n, f) in addition to neutron-capture reaction of individual target elements (La, Ce and Nd, respectively), its contribution was estimated and corrected for. As JP-1 has the highest U/LREEs ratios, collections reach 4 %, 21 % and 25 % for La, Ce and Nd, respectively. To make such a correction properly, U contents need to be known. We are now planning to determine U contents simultaneously together with REEs so that the proper contribution from U can be estimated.

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COSMOGENIC ^{45}Sc IN GIBEON IRON METEORITE BY RADIOANALYTICAL NEUTRON ACTIVATION ANALYSIS

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Meteorites and lunar rocks have cosmic ray induced stable and radionuclides called cosmogenic nuclides. These nuclides play important roles for determination of an irradiation age and a terrestrial age, estimation of cosmic ray intensity. Assuming that cosmic ray intensity was constant, contents of cosmogenic stable nuclides are proportional to period of cosmic ray irradiation. Noble gas stable isotopes are used to determine an irradiation age generally. Gibeon iron meteorite was found in Namibia in 1836 at first, and then total recovered fragment has been 21 tons. Honda et al. has been determined concentrations of cosmogenic nuclides such as stable noble gas isotopes and several radionuclides in many fragments [1]. They found fragments having different exposure age estimated by stable noble gas isotopes and classified fragments into 2 sub-groups based on their exposure ages. There are two possible reasons that Gibeon shows 2 different ages; 1) Gibeon has a multi-stages exposure history, and 2) a part of noble gases were escaped from the meteorite body during fall. Non-volatile stable cosmogenic nuclides may be helpful for looking into candidate 2, second possible mechanism. So we determined concentration of ^{45}Sc in several Gibeon fragments by RNAA. Iron meteorites have essentially no geochemical lithophile elements such as Sc. Thus ^{45}Sc should be mainly a cosmogenic origin. One to 2 g of fragments etched by dil.HNO3 were irradiated at JRR-4 T-pipe for 1 hour or JRR-3 HR for 2 hours. Irradiated samples were etched by dil.HNO_3 again to remove Sc contamination on their surface completely. Samples were dissolved in dil.HNO_3 with Sc carrier, and Fe was extracted by MIBK from 4M HCl solution. Iron remained in 4M HCl was reduced to Fe^{2+} followed by extraction chromatography using TRU resin column [2]. Sc eluted by 1M HCl from the resin was recovered as scandium tartrate. Chemical yields of Sc were determined by gravimetry after gamma-ray spectrometry. Chemical yields were about 40 -80%. Low chemical yield were probably resulted by addition of careless large amount of carrier. ^{59}Fe, ^{60}Co, and ^{192}Ir, whose activity were as same as natural ^{40}K, were contaminated in final Sc precipitates. In this study 7 ppt associated with 10% of relative error were able to be determined and a detection limit of Sc content assuming 2 g of sample, irradiation for 2 hours, and 80% of yield attains 0.4 ppt. Irradiating for more long time, a detection limit can be reduced. Contaminations of ^{59}Fe and ^{59}Co have to become smaller. In this sturdy 0.0064 – 0.11 ppb of ^{45}Sc concentrations were obtained. It is guessed that ^{45}Sc blank level is less than 0.001 ppb that is 200 times lower than one estimated by Wänke [3]. ^{45}Sc concentration in Gibeon fragments showed good correlation with 4He concentrations and no systematic difference among sub-groups was observed. Average atomic ratio of ^{45}Sc/^{4}He was 0.087 ± 0.043 (1σ). Furthermore this ^{45}Sc/^{4}He ratio is consistent with one observed in other iron meteorites, 0.054 ± 0.025 (1σ). Thus it was concluded that noble gases were not escaped from meteorite body during the fall.

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MASS-DEPENDENT AND MASS-INDEPENDENT ISOTOPE FRACTIONATIONS OF LEAD IN CHEMICAL EXCHANGE REACTION USING A CROWN ETHER

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Lead is a well-known element, in which ^{206}Pb, ^{207}Pb, and ^{208}Pb are the radiogenic nuclides of ^{238}U, ^{235}U, and ^{232}Th, respectively. The isotopic composition of Pb in natural samples therefore varies widely depending on the U/Pb and Th/Pb ratios in the samples. Naturally occurring Pb isotopes consist of three isotopes mentioned above and an isotope ^{204}Pb. The isochron by using ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb gives us valuable information on the formation and aging of samples [1]. In order to obtain the accurate isotopic data, any isotope fractionations classified to be non-radiogenic should be clarified. It is of interests whether chemical reactions between Pb species cause isotope fractionation or not, especially the mass-independent isotope fractionation.

Lead isotopes were fractionated by the liquid-liquid extraction technique with a crown ether. This method is effective to see possible isotope fractionation of Sn [2], which is a congener of Pb. After purification by ion-exchange chemistry, the isotope ratios of ^{m}Pb/^{206}Pb (m: 204, 207, and 208) were measured precisely by multi-collector inductively coupled plasma spectrometry (MC-ICP-MS) at the "Pole Spectrometry Ocean" (PSO) of Brest. Isotope fractionations >0.1‰ have been found. With the increase of acidity, the isotope enrichment factor was found to decrease. At a high acidity region, the isotope enrichment factor of the odd atomic mass isotope (^{207}Pb) showed a mass-independent property compared to the even atomic mass isotopes $^{(204\mathrm{Pb}}$, ^{206}Pb, and ^{208}Pb). The mass-independent isotope fractionation should be attributable to the nuclear field shift effect [3].

The conventional mass-dependent theory of isotope fractionation [4] has been reconsidered and extended to include correction terms to account for nuclear properties, i.e., nuclear mass, nuclear size and shape, and nuclear spin [3]. The nuclear field shift effect, which results from the isotopic change in the nuclear size and shape (nuclear volume), is the most possible origin of the mass-independent isotope fractionation in chemical exchange reactions.

In order to check the validity of the isotope enrichment factor obtained, we performed the molecular orbital calculations for related Pb complexes. The equilibrium constant of the isotope exchange reaction was theoretically obtained, as the reduced partition function ratio (RPFR) of isotopologs. As the mass-independent isotope effect, the contribution of the nuclear volume was estimated by employing the numerical multiconfigurational Dirac–Coulomb Hartree–Fock (MCDCHF) method.

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STUDY ON ANTIMONY POLLUTION FORM IN SOIL AROUND SMELTER BY MEANS OF INAA

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Antimony (Sb) is one of natural occurring trace elements in soil, but it is being identified as a pollutant by increasing its usage. Flame retardants, paints and pigments are important industrial products, and 13,279 t of antimony trioxide (Sb_2O_3) was in demand at 2006 in Japan. It is pointed out that these important products, flame retardants, paints and pigments, are end up in the garbage and loaded in the environment. Antimony is categorized as one of items to be monitored in Japan, and the guideline values of antimony are under 0.02mg/L and 0.015mg/L for the public water quality and the tap water quality, respectively. As just described, antimony is needed to be studied about its behavior in the environment because of its large amount of usage and the strict guideline values. In this study we attempt to analyze characteristics of antimony pollution in soil environment and clarify its behavior. The soil sample was collected around an antimony smelter in Japan where health hazards had been occurred in 1970's. The collected soil was dried in air and sieved through a 2mm sieve. This pretreatment soil was then sieved through 2000, 1000, 850, 425, 250, 106, 75, 44μm sieves, and 9 fractions of the soil sample were prepared. Instrumental Neutron Activation Analysis (INAA) was conducted for determination of antimony concentration in these soil samples. About 100 mg soil was sampled from each fraction, and two samples were prepared from one fraction. These two samples from one fraction were into separate capsule (capsule A and Capsule B). These soil samples were irradiated at HANARO (High-flux Advanced Neutron Application Reactor) in KAERI (Korea Atomic Energy Research Institute) together with city waste incineration ash BCR-176(Commission of The European Communities) for comparison standard. Using the neutron irradiation facility of NAA1 (thermal neutron flux: 3.9×10^{13} n/cm^2/s), two capsules were irradiated sequentially. Irradiation time was 10 minutes for the each capsule, and after about one month for cooling, γ-ray spectrometry was conducted. Concentration of each element was calculated by using comparison method. Comparing other elements like iron (Fe) or europium (Eu), the antimony pollution forms are discussed.

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HEAVY METAL ELEMENTS IN TOILETRIES ANALYZED BY INAA AND ICP-MS

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Chief ingredients of toiletries are organic compounds. Recently, many toiletries claiming inclusion of platinum (Pt), silver (Ag) and gold (Au) as additives are sold in ordinary cosmetics shops. These toiletries were analyzed by instrumental neutron activation analysis (INAA) method and Inductively Coupled Plasma Mass Spectrometer (ICP-MS) method. The concentrations of the Pt in the toiletries were from 1 to 80 ppm. The lower detection limit value of Pt of the standard sample was 1 ppm under the present experimental condition of INAA. Because sodium in toiletries was irradiated with very high sensitivity, the background level was different in each toiletry. So, some toiletries which were claimed to contain Pt in the labels by the makers were of less Pt concentrations than the detection limit contrary to the claiming in the label. On the other hand, there were a few toiletries with rather a large amount of Ag although no mention of Ag as an additive. These non-indicated Ag were regarded as impurities of the added Au. The concentrations of the non-indicated Ag were higher than that of the indicated Ag. Heavy elements analyses with ppb levels were possible without preprocessing of the samples in the INAA method. In the ICP-MS method, some preprocessings are required although the sensitivity is very high. Very small amounts of Pb, Sr and Zn were detected in 2 kinds of toiletries out of 5 kinds analyzed. It is considered that the elements such as Ag were included in toiletries as impurities of the added heavy metal element.

PO-2-11-12 16825

DEPOSITION IN LUNG AND TRANSLOCATION TO SECONDARY TARGET ORGANS AFTER INTRATRACHEAL INSTILLATION OF NANO-CERIA

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The wide application prospects of nano-ceria call for urgent assessment of its environmental and biological safety. However, most of the previous work focused on the cell level performance of nano-ceria, little was known about the subsequences of nano-ceria exposure on the whole-body and organ level. In the present work, radiotracer technique was employed to study the pulmonary deposition and translocation to secondary target organs after nano-ceria was intratracheal introduced to Wistar rats. The results of whole-body distribution showed that intratracheal instilled nano-ceria could pass through the alveolar-capillary barrier into systemic circulation within 5 min, but the ceria content in blood remained at extremely low level; 63.9±8.2% of delivered nano-ceria remained in lung by 28 days postexposure, and the left part of given dose was mainly contained in feces, liver and spleen; a comparison test showed that little of nano-ceria administrated orally was absorbed in GI tract and nearly 100% of the given dose were excreted in feces by 3days postexposure. The data quantitatively demonstrated that the translocation of nano-ceria from the respiratory epithelium towards circulation did occur after the nano-ceria was deposited in the alveolus, but in a quite slow way. The results suggested that the effect of nano-ceria exposure, even at low concentration, should be assessed because of the potential lung and systemic cumulative toxicity of the nanoparticles.

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INVESTIGATION OF MINTERALS DISTRIBUTIONS IN BONE OF TIBOLONE THERAPY BY SYNCHROTRON X-RAY FLUORESCENCE MICROSCOPY

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The most common treatment, in order to combat the symptoms of menopause, is the hormone replacement therapy which gives artificial supply of estrogen and progesterone allowing the body to function with fewer menopausal symptoms. However, this long-term therapeutic administration has demonstrated disadvantages such as an increase of cancer incidence on the endrometrium and heart diseases. Nevertheless, other alternative appears, such as tibolone treatment. Tibolone was first produced by Organon (West Orange, NJ, USA) as synthetic steroid with estrogenic, androgenic, and progestagenic properties. It has been used primarily for the prevention of postmenopausal osteoporosis and treatment of climacteric symptoms. This great advantage against hormone replacement therapy is its specific tissue action which performs differently in each part of the organism. In this way, tibolone has almost no action on breast and endometrium locations where estrogens generally have action. In this work, in order to evaluate the effects of a long-term administration of tibolone, the µXRF-SR imaging technique was used. In this context, it was possible to investigate qualitatively and quantitatively bone mineral content such as calcium and strontium in bone samples, specially its distribution on bone microarchitecture. It was possible to observe that bone animals which received tibolone treatment presented more mineral concentration and more disorganized microarchitecture than ovariectomized bone animals.

THE ZINC DISTRIBUTION IN BONE

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Zinc (Zn) is an essential element that can be found in bones, such as calcium and phosphorus. It seems to have effects on growth, bone turnover and mineralization making its relationship with bones still opening. Zn is one of the most abundant nutritionally essential trace elements in human body and it is known to be necessary for normal bone metabolism. It is found in all body tissues with 85% of the whole body zinc in muscle and bone, 11% in the skin and the liver and in the remaining in all the other tissues. The participation of trace minerals in normal development and maintenance of the skeleton is related to their catalytic functions in organic bone matrix synthesis. This mineral regulates secretion of calcitonin from thyroid gland and influences bone turnover. Its deficiency causes reduction in osteoblastic activity, collagen and chondroitin sulfate synthesis and alkaline phosphotase activity.

It is known that deficiency of ovarian hormone in menopause stimulates bone loss. Ovariectomy also causes osteoporosis due to the lack of estrogen. Many in vitro and in vivo studies of ovariectomized animals have been reported that Zn has an anabolic effect on bone metabolism by inhibiting bone resorption, stimulating bone formation and mineralization. Its mineral has a structural role, bound to fluoride in the hydroxyapatite. Some other results reported that zinc plays an important role in bone metabolism. As an example, it can be said that estrogen support in post-menopausal women decreases zinc discharge and thus being recommended the use of zinc as a new marker in the determination of changes in bone metabolism.

The x-ray microfluorescence (μXRF) is an analytical technique based on the elemental local excitation and microscopic analysis of the region of interest. Through this technique it is possible to determine the elemental concentration and the distribution of the elements on a sample surface. The advent of synchrotron radiation (SR) has added a new dimension to the use of x-rays in imaging. Its brilliance and brightness allows high efficiency for trace.

The goal of this study is, by μXRF with SR analysis, to characterize bone samples, with and without osteoporoses, in both trabecular and cortical regions. For that purpose, it was used an XRF beam line at the Synchrotron Light National Laboratory (Campinas, Brazil).

The results show that the profile of the zinc distribution and its concentration on femoral heads are strongly related to the associated pathology. The images show that the Zn distribution is heterogeneous and its preferential location is in trabecular regions which is more metabolic active than cortical bone.

VERTICAL DISTRIBUTIONS OF ^{228}Ra AND ^{226}Ra IN THE JAPAN BASIN; IMPLICATIONS FOR WATER CIRCULATION AND RESIDENCE TIME

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The Sea of Japan is surrounded by the Eurasian continent and the Japan Islands, and is connected to the Pacific and other marginal seas by the very shallow Tsushima, Tsugaru, and Soya Straits (<~150 m of depth). Therefore, the deep water, so-called the Proper Water of the Sea of Japan, has no influx from a surrounding sea, indicating unique vertical water circulation [1]. ^{226}Ra ($t_{1/2}$ = 1600 y) and ^{228}Ra (5.75 y) of seawater have been used as powerful tracer for studying the migration of water masses as well as other nuclides such as thorium isotopes, ^{210}Pb, ^{137}Cs, and ^{90}Sr [2]. However, standard γ-spectrometry for measuring ^{228}Ra of deep seawater usually requires very large volumes (hundreds to thousands of liters) because of its low activity and previously reported data are not sufficient to allow investigating the details of the vertical distribution of ^{228}Ra in oceans. In this study, by employing low-background γ-spectrometry combined with minimal radiochemical processing, we analyzed seawater samples from the Japan Basin, in the east of the Sea of Japan, for ^{226}Ra and ^{228}Ra. Low-background γ-spectrometry was performed using well-type Ge-detectors, which are located at the Ogoya Underground Laboratory, Japan (equivalent to a water depth of 270 m) [3]. Detailed explanations of these experimental procedures were presented elsewhere [4]. γ-Peaks for ^{228}Ra measurement (^{228}Ac; 338 and 911 keV) on a blank sample, which was performed our experimental procedures on 50 L of distilled water, were "not detected" level. Therefore, we corrected only least Ra-contaminated Ba-reagent blank, which accounted for <1% ^{228}Ra for our water samples. The ^{226}Ra activity of the water samples from the Japan Basin gradually increases from surface to the Deep Proper Water (1.5-2.3 mBq/L). The ^{228}Ra activity of the water exhibits steep gradients with depth from the surface to the Upper Proper Water (1.8-0.2 mBq/L), and short-lived ^{228}Ra is continuously delivered to the Deep Proper Water by the active water circulation before it radioactively decays. This clarifies the vertical circulation of water masses and the residence time of the Proper Water.

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SEPARATION SCIENCE AND INSTRUMENTAL APPROACHES IN RADIOANALYTICAL CHEMISTRY

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Trace and ultra trace analytical techniques have achieved/even now trying to achieve lower detection limits to meet the requirements of scientific applications in almost all branches/fields of life and science. Reference materials play an important role during trace analysis. The basic purpose of their use is to validate the measurement process. Standard Reference Materials (SRMs)/Certified Reference Materials (CRMs) are playing most crucial roles in validating the analytical data. Reliability of the data using analytical techniques therefore depends on the reliability of the composition of these comparators. For instance, in nuclear industries, materials used in it have stringent specifications and before putting them in reactor, characterization of these materials is essential. Such is the case for some high purity materials like gallium, arsenic used in the preparations of semiconductors. Even for environmental/life-science related materials, medicines including herbal/ayurvedic preparations, forensic exhibits meticulous analytical data is required. The use of direct modern instrumental approach is heading leaps and bounce speed. These developments in instruments has risen the limits of detection to several folds, but in many instances, direct instrumental approach may/could be a wrong choice for trace analysis**.** Does the need for a simple wet chemistry still exist in analytical chemistry? -is a big question mark in today's PUSH BUTTON era. Employing a simple separation step followed by suitable instrumental approach has been demonstrated during this work to arrive at more meaningful data during analysis of typical matrices like USGS RMs, uranium, thorium, gallium, arsenic, selenium, scandium, and environmental matrices. These separation procedures improves S/N ratio, overcomes effects due to matrix, salt concentrations and other problems of direct instrumental approaches including nuclear technique and the details are discussed in this paper.

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APPLICATION OF CONTINUOUS HEATING METHOD BY THERMAL IONIZATION MASS SPECTROMETRY FOR MEASUREMENT OF ISOTOPE RATIOS OF PLUTONIUM AND URANIUM IN TRACE AMOUT OF MOX SAMPLE

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The environmental sample analysis for the strengthened safeguards system of the IAEA was carried out to find undeclared nuclear activities and to detect undeclared nuclear facilities. Recently it becomes important to develop analytical technique of small particle consisted of MOX, use of which has been increased as a fuel of a nuclear power plant in the future.

In this study, we report a new method for simultaneous measurement of isotope ratios of plutonium and uranium in trace amount of MOX sample. Continuous heating method by thermal ionization mass spectrometry was applied to the measurement, which was developed for isotope ratio measurement of trace amount of U in our laboratory. Features of this method were that (1) high intensities could be held on continuously with increasing temperature of an evaporation filament, (2) isotope ratios were calculated precisely from the higher intensities observed during the measurement and (3) standardization of measurement condition such as heat slope and isotope ratio calculation was achieved. These allowed us to obtain precise results in independence of sample size and operator's experience.

Mixture samples containing 1 pg of Pu (SRM-947) and 1 pg of U (U-350) were used in order to optimize measurement condition. Masses (*m/z* values) of 235, 238, 239 and 240 were measured dynamically using the SEM with mass jumps and integrated time for each mass is 2 seconds for 235 and 240 and 4 seconds for 238 and 239. In this continuous heating method, heat slope (Heating rate) of the evaporation filament was optimized as follows; 200 mA/min during 0 – 1800 mA and then 250 mA/min until 5000 mA. The results of the isotope ratios (240Pu/239Pu and 235U/238U) were in good agreement with the certified values within the standard deviation. This method enabled us to the isotope ratio measurement without chemical separation of U and Pu. The result of 238Pu/239Pu ratio will be also presented.

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ISOTOPE CORRELATIONS FOR ALPHA SPECIFIC ACTIVITY AND ISOTOPIC COMOOSITION OF PLUTONIUM IN HIGH BURNUP PRESSURIZED WATER REACTOR SAMPLES

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Isotope correlations for alpha specific activity and isotopic composition of Pu have been derived based on the Pu data obtained by an alpha spectrometry and a thermoionization mass spectrometry [1]. The correlations for the isotopic composition of Pu in high burnup PWR samples were derived with empirical fittings using the techniques already reported. Correlations among the alpha activity ratios of ^{238}Pu/(^{239}Pu+^{240}Pu), the alpha specific activities of Pu and the atom % abundances of Pu isotopes were derived for the plutonium samples. Using the alpha activity ratios of ^{238}Pu/(^{239}Pu+^{240}Pu) which were determined by an alpha spectrometry, the alpha specific activities of Pu as well as the atom % abundances of the plutonium isotopes in the unknown samples were calculated. The calculated alpha specific activities of Pu agreed with those determined by an experiment within 2%, and the atom % abundances of the Pu isotopes agreed within a range of 4 ~ 7 % according to the isotopes, respectively. In addition, a correlation between the fuel burnup and the alpha activity ratio of ^{238}Pu/(^{239}Pu+^{240}Pu) was elucidated at a range of the burnup from 35.6 to 62.9 GWd/MtU. A fairly good correlation between the fuel burnup and the alpha activity ratio of ^{238}Pu/(^{239}Pu+^{240}Pu) was obtained in the experiment.

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PO-2-11-19 15060

ELEMENTAL ANALYSIS OF FLY AND BOTTOM ASHES FROM A COAL POWER PLANT BY NEUTRON ACTIVATION ANALYSIS

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Coal has been used for 40% of the total electric power production in Korea. Obviously, by-products such as fly ash (FA), bottom ash (BA), and boiler slag through coal combustion are being generated. While 80% of fly ashes have been reused, most of the bottom ashes have been land-filled in the ash pond. In this work, the inorganic elemental contents in the fly and bottom ash from a coal power plant were determined by an instrumental neutron activation analysis. Coal ash samples were collected from the biggest thermal power plant complex in Korea. The samples were analyzed by using the NAA facilities in the HANARO research reactor of the Korea Atomic Energy Research Institute. 34 elements were analyzed in the samples and certified reference materials (NIST SRM 1633b, 1632c) were used for the analytical quality control.

PO-2-11-20 15901

MEASUREMENTS OF DETECTION LIMITS FOR TRACE ELEMENTS BY MULTIPLE PROMPT GAMMA-RAY ANALYSIS

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Multiple prompt gamma-ray analysis (MPGA) is a powerful technique for trace element analysis [1, -4]. In MPGA, we apply a multiple gamma-ray detection method to prompt gamma-ray analysis [5]. MPGA has the characteristics of high-sensitivity and high-precision. Furthermore, MPGA is suitable for multi-elemental nondestructive analysis. Therefore, this method is useful for trace element analysis of scarce samples and industrial materials. A detector system for multiple prompt gamma-ray measurement was constructed at the neutron guide hall of JRR-3 reactor of Japan Atomic Energy Agency [6]. The system consists of eight Clover Ge detectors and BGO Compton suppressors. We performed MPGA for several standard samples, in order to investigate the detection limits for trace elements. In MPGA, two or more cascade gamma-rays are detected coincidentally by several gamma-ray detectors. Event composed of pairs of gamma-rays are collected in the experiment and are added to a two-dimensional gamma-ray spectrum, which is a histogram of gamma-gamma energy correlation. From analyses of the two-dimensional gamma-ray peaks, the quantities of trace elements in the samples can be determined. Based on the results, we present detection limits for about 40 elements with the MPGA system. This research was partly conducted as the Practical Application Research and supported by JST Innovation Satellite Ibaraki. The authors would like to thank Director Katsutoshi Goto and staff for their assistance.

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REPROCESSING OF RESEARCH REACTOR NUCLEAR FUEL BASED ON PYROCHEMICAL SEPARATIONS TECHNIQUE

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Treatment of spent nuclear fuel has received substantial attention over the last decade. At Idaho National Laboratory pyrochemical separations is used to treat irradiated fuel elements from the Experimental Breeder Reactor II (EBR-II). EBR-II is a sodium-cooled fast reactor at the Materials and Fuels Complex of the Idaho National Laboratory which was shutdown in the late 1994 after 30 years of operation. It used uranium-10 wt% zirconium metallic fuel alloy enriched to 67-78% uranium-235. Pyrochemical technology is applied to discharged spent fuel to separate the uranium from other fuel components. The experience and data obtained from this project may be used to treat high-density low enriched uranium (LEU) research reactor nuclear fuel. This is consistent with the Advanced Fuel Cycle Initiative (AFCI) within the U.S. Department of Energy's Office of Nuclear Energy, Science and Technology, to explore applications of pyrochemical separations to various fuel types. Therefore, pyrochemical processing of research reactor fuel is the focus of this paper.

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WATER DIFFUSION IN FLYOROPOLYMER-BASED FUEL-CELL ELECTROLYTE MEMBRANES INVESTIGATED BY RADIOACTIVATED-TRACER PERMEATION TECHNIQUE

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During the operation of a polymer electrolyte membrane (PEM) fuel cell, water is transported to cause a non-uniform water distribution in a PEM, which is directly related to cell performance. Accordingly, we investigated water transportation phenomena in our original PEMs prepared by radiation-induced grafting of styrene into crosslinked-polytetrafluoroethylene (PTFE) films and the subsequent sulfonation [1]. For this purpose, the self-diffusion coefficient of water, D_W, was evaluated by water-permeation experiment using tritium-labelled-water (HTO) as a radioactive tracer [2].

Fig. 1 represents the D_W values as a function of the ion exchange capacity (IEC). For the PEMs we prepared, D_W showed an increasing trend with the IEC. At the same IEC, the crosslinked-PTFE-based PEMs exhibited lower D_W compared to that in the non-crosslinked-PTFE-based ones. However, when D_W was re-plotted against the water volume fraction in a PEM, φ, the effect of PTFE crosslinking disappeared. In other words, D_W was determined by only φ. This is interpreted as follows: expansion of water-filled hydrophilic regions would allow water molecules to move faster. Interestingly, a commercially-available Nafion112 membrane exhibited the highest D_W of all the measured samples despite its low IEC and φ. The lower D_W in our PEMs is probably attributed to the geometry of hydrophilic regions phase-separated from the surrounding hydrophobic polymers. It is reasonable to consider that hydrophilic hydrophobic phase-separation morphology is not so distinct, thereby forming narrower and more branched water-transport channels than those in Nafion. The resulting tortuous structures should reduce D_W [2].

For comparison, non-radioactive $H_2{}^{18}O$ was used as a tracer to obtain the self-diffusion coefficient, $D_W(^{18}O)$, in the same way. In bulk water, $D_W(^{18}O)$ was lower than D_W because a $H_2{}^{18}O$ molecule had the smaller principal moment of inertia [3]; this was also true of the Nafion result (see Fig. 1). On the contrary, no significant difference appeared between D_W and $D_W(^{18}O)$ in the cPTFE PEMs. We considered the possibility that T in an HTO molecule might exchange with a proton (H^+) released from a sulfonic acid group to give T^+. Such a T/H^+ isotopic exchange is likely to have influence on the behavior of D_W.

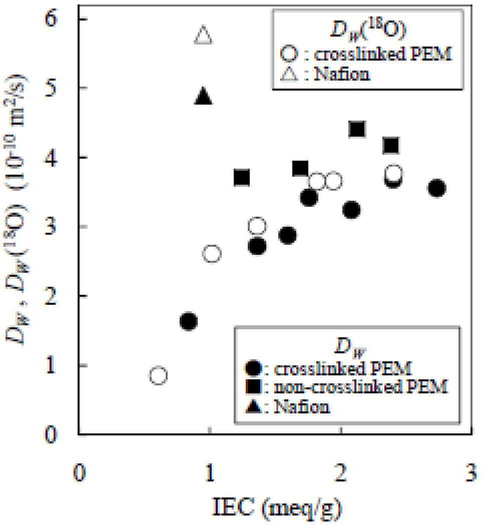

Fig. 1: Plots of D_W and $D_W(^{18}O)$ vs. IEC for the PEMs based on crosslinked- and non-crosslinked PTFE films as well as Nafion112.

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SYNTHESIS OF WATER-SOLUBLE ENCAPSULATED-RADIOISOTOPE FULLERENES

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Water-soluble fullerene derivatives have been investigated to date mostly within the framework of biological and medical applications. We investigate to trace the synthesis process of water-soluble encapsulated-radioisotope fullerenes using the recoil of nuclear reaction.

In order to produce $^{75}Se@C_{60}$, about 60 mg C_{60} fullerenes powder was mixed homogeneously with about 60 mg of As_2O_3 and used to the target material. Proton irradiation with beam energy of 13 MeV was performed at the TANDEM in JAEA. Radioisotopes of ^{75}Se can be produced by $^{75}As(p,n)^{75}Se$ reactions. The beam current was typically 1 μA and irradiation time was about 2 h. The irradiated fullerene samples were dissolved in CS_2 after being filtrated to remove insoluble materials through a membrance filter (pore size = 0.2 μm). The separation of the $^{75}Se@C_{60}$ from the solved sample was achieved by two steps HPLC which are the HPLC processes on 5PBB and Buckyprep columns. Toluene solutions of isolated $^{75}Se@C_{60}$ with C_{60} were vigorously vibrated with saturation KOH aq containing few drops of TBAH (10 % in water) as catalyst at room temperature. The reaction (sharking) times were 5 - 480 minutes. The reaction mixture was filtrated by 0.2 μm PTFE filter. The precipitate was rinsed with methanol to ensure the removal of the catalyst and KOH. The rinsed precipitate was dissolved in 3 mL distilled water for 7 hours. The resultant brown solution was the passed down a Sephadex G25 size-exclusion gel chromatography column using distilled water as the eluent. All products of reaction process were traced 264.7 keV □-emission of ^{75}Se by an HPGe detector.

We obtained which the activity ratios of ^{75}Se in three phases (Organic phase, KOH aq. phase, and precipitate) as function of reaction time as shown in Fig.1, and which the fraction yields of ^{75}Se in dissolved precipitate through a Sephadex G25 as function time of reaction time. The reaction time was changed the distributions of the activity to a KOH aq. phase and precipitate. As reaction time is long, the activity exists in the KOH phase, and the fraction yields of $^{75}Se@C_{60}$ increased. The chemical behavior corresponded to the $^{153}Sm@C_{82}$ data1).

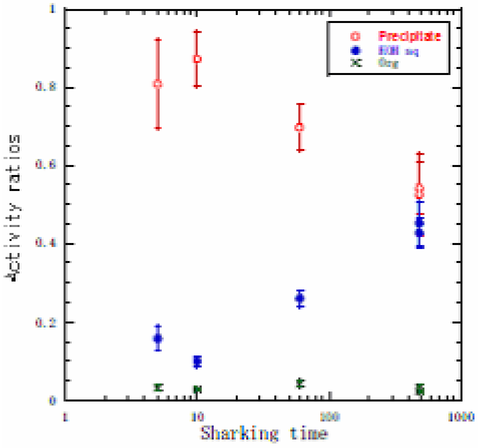

Fig. 1 Tthe activity ratios of ^{75}Se in three phases as function of reaction time.

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PO-2-11-24 14942

THE EXTRACTION OF PAST ENVIRONMENTAL INFORMATION USING ^{137}Cs AND SOME ELEMENTS IN TERRESTRIAL CARBONATE DEPOSITS

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Terrestrial carbonate deposits with a banded layer structure can be good tools for the extraction of past environmental information on global and local scales. The absolute age dating is most important for the reconstruction of an environmental chronicle. The terrestrial carbonate deposits (Tufa) was collected at Hirao-dai Plateau in Fukuoka. Tufa has wide banded layers in which the growth rates are about a few mm a year. The activity of ^{137}Cs that was a global or local fallout radionuclide was measured in each layer of Tufa sample. The absolute age was determined by the numbering of a banded layer and ^{137}Cs activity profiles. The trace of the atomic bombing at Nagasaki was detected. The growth rate of the Tufa is related to the climate of the year. The variations of a depositional condition of tufa sample were checked by some metal concentrations determined by neutron activation analysis. Neutron activation analysis was performed at JRR-3 and JRR-4 reactor, JAEA. The concentration of the elements in samples was determined by comparative method using JB-1 as a standard. The elements, Al, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Mg, Mn, Na, Sc, Se, Sm, Ta, Th, Ti, V and Yb, were determined. The relationship between the variation of environmental condition and the historical event at Hirao-dai was discussed using these metal concentration profiles.

PO-2-11-25 14934

DEVELOPMENT OF CLASSIFICATION TECHNOLOGY FOR THE CHARACTERIZATION OF RAW MATERIALS AT PRODUCTION KILMS IN BAEKJE PERIOD

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Neutron Activation Analysis (NAA) has been applied to provenance studies in ancient potteries. However, most cultural heritages analyzed by NAA were of the ancient earthenware in Korea. Besides, scientific research for ancient potteries such as celadon, Pun-cheong and whiteware were oriented to the analysis of major constituents and physical properties. This study aimed to determine the trace elemental contents of the crucible, pottery and roof tiles excavated from the kiln of production site by NAA and to classify their origin. 51 samples consisting of 27 crucibles, 14 pottery, and 10 roof tile samples, were selected and analyzed by Instrumental Neutron Activation Analysis (INAA) and 25 elements were determined. Four factors were determined by principal component analysis (PCA) and discriminant analysis was carried out to classify the correlation of raw materials with the selected samples.

PO-2-11-26 20869

PREPARATION OF LABELED PORPHYRIN COMPOUNDS FOR PET AND GAMMA CT

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Recently, positron emission tomography (PET) has been remarkably developed for visualizing the distribution of a radionuclide in the human and animal's body[1]. Now the system is widely used for the diagnosis of cancer. Clinical application of PET has been made possible with the development of ingenious techniques for rapid synthesis of radiopharmaceuticals, suitable for in vivo studies, using cyclotron within a medical complex. We selected to produce the radioisotope-labeled hematoporphyrin for the PET and gamma CT although the radio-pharmaceutical mostly used is the 18F-labeled fluoro-deoxy-glucose which is similar to glucose in behavior.

We synthesized ^{52}Fe($T_{1/2}$=8.28h), ^{62}Zn($T_{1/2}$=9.3h) and ^{124}I($T_{1/2}$=4.18d) which were positron emitters by the ^{52}Cr(^{3}He,3n)^{52}Fe, ^{62}Cu(p,n)^{62}Zn and ^{124}Te(p,n)^{124}I reaction, respectively with the AVF cyclotron at Research Center for Nuclear Physics, Osaka University. The excitation functions of the interested nuclear reaction were measured by means of a stacked-foil method. The most relevant beam energy of the nuclear reaction producing the interest nuclide were decided. Further, the recoiled range of the produced nuclides was measured by a catcher foil technique for the decision of optimum thickness of the target.

We produced the ^{65}Zn-labeled hematoporphyrin to measure gamma-ray computer tomography in vivo. Zinc-65 nuclide was produced by the ^{nat}Cu(p,xn)^{65}Zn reaction with the AVF cyclotron and the Cu target was dissolved into HNO_3 solution. The $^{65}Zn^{2+}$ ion was separated from Cu^{+} ion by means of anion exchange column separation. Further, $^{65}Zn^{2+}$ was dissolved into methanol and reacted with a hematoporphyrin. The radioactivity of ^{65}Zn was measured by means of gamma-ray spectrometry with a Ge detector. The ^{65}Zn-labeled hematoporphyrin was introduced into the mouse in which tumour was previously grown up. The gamma-ray imaging of tumour was obtained by the Electron Tracking Compton Camera(ETCC) at the Graduate School of Medicine, Kyoto University. In the following Fig.1 the schematic diagram of the preparation of radioisotope-labeled hematoporphyrin is shown. Finally, the compound is introduced into human and animal's body, and PET and gamma-CT image are measured. We will discuss for the target materials, the variety of beam and energy, the chemical separation method, the chemical reaction with radioactive tracer et al..

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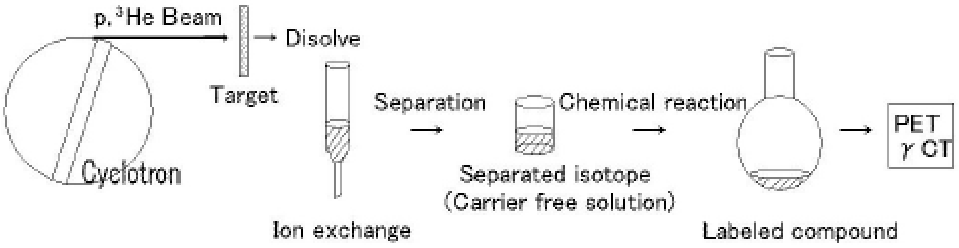

Fig.1. Schematic diagram of the preparation of the labeled compound

PO-2-11-27 20469

Ra ISOTOPES IN Na-Cl TYPE GROUNDWATERS FROM DEEP WELLS IN THE COSTAL AREAS OF HIMI CITY, TOYAMA PREFECTURE, JAPAN

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The distributions of radionuclides, especially U- and Th-series radionuclides, in groundwater provide important insights into the geochemical process such as the rate of water-rock interaction and mobility of pollutant nuclides. Radium isotopes, which are more mobile element in saline water, are generally considered to be supplied from surrounding rocks. However, it was reported that ^{228}Ra/^{226}Ra activity ratios in groundwater had higher values than ^{232}Th/^{238}U activity ratios in rocks, indicating that Th isotopes at water-rock interface may play an important role for radium isotope transport. The purpose of this study is to clarify the transport processes of radium isotopes in deep aquifer from the point of activity ratios among U, Th and Ra isotopes in both groundwater and rock samples. Nine groundwaters from deep wells and one natural spring water were collected at Himi City in Toyama Prefecture, Japan (Fig. 1).

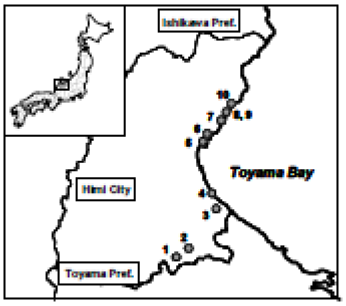

Fig. 1 Sampling locations of water samples

Drilling cuttings were also collected at No. 10 well. Waters sampled were approximately neutral and Na-Cl type. The concentrations of ^{226}Ra in water ranged from 2.2 to as high as 1970 mBq/kg. The ^{228}Ra/^{226}Ra activity ratios also varied with a wide range from 0.93 to 11.7, and this high activity ratio led us to very interesting results for better understanding the transport processes of Ra isotopes into water phase. Uranium-238 concentrations in water were extremely low with a maximum value of 0.23 mBq/kg, indicating that the groundwaters were trapped in reducing conditions. This finding was consistent with the extremely low concentration or absence of SO_4. The ^{232}Th/^{238}U activity ratios of bulk rock ranged from 0.23 to 2.5, whose values were obviously lower than ^{228}Ra/^{226}Ra activity ratios (11.6). This observation might imply the occurrence of other Ra isotope source at water-rock interface, which has different ^{232}Th/^{230}Th (^{232}Th/^{238}U) activity ratio from bulk rock phase although there are other factors considered. Now, extraction experiments using rock samples are running to assess the distributions of Ra, Th and U distribution at water-rock interface, and the results will be discussed.

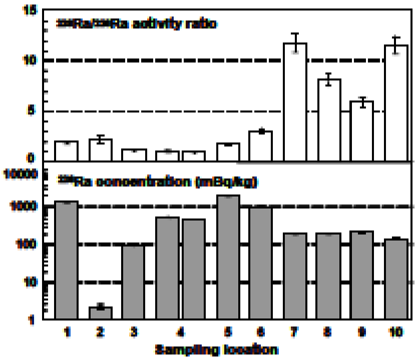

Fig. 2 ^{226}Ra contents and ^{228}Ra/^{226}Ra activity ratios of water samples

PO-2-11-28 18688

STRUCTURAL CHANGE OF MULTIWALLED CARBON NANOTUBES THROUGH γ-RAY IRRADIATION

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Purified multiwalled carbon nanotubes (MWCNTs) were irradiated by 60Co γ-ray with different doses. The Structural change of the MWCNTs was revealed by high-resolution transmission electron microscopy and Raman spectroscopy. It was found that under γ-ray irradiation some amorphous structure homogeneously covers the inner tube walls with graphite structure in irradiated MWCNTs. Moreover, the amorphous structure continuously proceeds and the graphite structure is reduced during the γ-ray irradiation until the irradiated MWCNTs become amorphous nanowires with a hollow structure.

Based on the interaction between photons and carbon nanotubes, the structural transformation process and corresponding mechanisms are discussed. In MWCNTs the collision of a photon with a carbon atom will result in displacement of the atom, i.e. formation of a vacancy (single- or multi- vacancy) and a number of primary knock-on atoms which, if their energy is high, leave the tube or displace other atoms in the MWCNTs. If their energy is low, they can adsorb onto the tube walls. These adsorbed atoms play the role of interstitials. All displaced atoms can be sputtered from the MWSNTs.

The carbon atoms sputtered from the MWCNTs can further create some damage in a nearby MWCNTs or absorb onto its surface. Along with the simple defects, a number of more complex defects can be formed. The behavior of complex irradiation-induced defects is governed in part by annealing and diffusion of original defects-vacancies and interstitials. The γ-ray irradiation induced structural transformation of MWCNTs was a unique graphite to amorphous structural transition from the outer walls to the inner walls of the irradiated MWCNTs due to the removal of carbon atoms by knock-on displacements.

PO-2-11-29 16584

METEOROLOGICAL FACTORS PRODUCING VARIATION OF TRITIUM CONCENTRATIONS MEASURED IN FUKUOKA, JAPAN

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Tritium is a radioactive isotope of hydrogen with 12.32 years half-life and is produced naturally in the upper atmosphere by cosmic radiation. Tritium, in the form of HTO, has been incorporated into a hydrological cycle and has been used as a tracer of water movement for many years. Japan is located on the eastern edge in Eurasia continent and is usually covered with air mass from the Pacific Ocean in summer and from the Eurasia continent in winter. We have measured tritium concentrations of environmental waters. In this presentation, we show the recent tritium concentrations and discuss the meteorological factors which produce the variation of tritium concentration. Tritium concentrations of rain and river water in Fukuoka, Japan were analyzed by low background liquid scintillation counting combined with enrichment of tritium by electrolysis using solid polymer electrolyte. The rain water samples were collected with a plastic tray placed on a roof of a building at Kyushu University for the period from May 2005 to April 2009. The river water samples were collected in two places (upper and lower stream) of Tatara river system every month for the period from April 2007 to March 2009. Tritium concentration of rain vary between 0.23 and 2.07 Bq/L with an average of 0.78 Bq/L (n=93). A seasonal variation is observed for tritium concentration: high in winter and spring, low in summer and autumn. The detailed examination of the seasonal variation using the back-trajectory analysis suggests that rain clouds arrived at Fukuoka passed through the Eurasia continent have higher tritium concentration than those passed through the Pacific Ocean. The tritium concentrations of rain seem to be determined by migration pathway of rain clouds rather than seasonal variation. Tritium concentrations of river vary between 0.39 and 0.83 Bq/L with an average of 0.54 Bq/L (n=46). Although the rain, which is a source of river water, showed the seasonal variation in tritium concentration, the river water has lower tritium concentration than rain and does not show any cyclic variation. The river waters collected in the upper stream tend to have higher tritium concentrations than the paired sample collected in the lower stream. These facts suggest that there exists other water source controlling tritium concentration in the Tatara river system.

PO-2-11-30 14995

CYCLIC NEUTRON ACTIVATION ANALYSIS OF FLUORINE IN COMMERCIAL TEA AT SHENZHEN, CHINA

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It is well known that proper amount of fluorine could prevent dental caries and osteoporosis. However, long-term exposure under excessive fluorine could lead to chronic fluorine intoxication. Tea tree is a kind of plant rich in fluorine as it selectively absorbs fluoride from soil and air. Tea leaves, containing about 87-98 % fluorine of tea tree, are the major accumulation organs. Besides, the older the tea tree is, the more fluorine they contain. As one of the most common beverages in the world, tea can be classified into non-fermented green tea, partially fermented oolong tea, and fully fermented black tea and Pu-erh tea. Consumption of tea has been closely related to many health benefits, e.g.cancer prevention. Therefore, exposure to fluorine via tea and associated health benefit or risk should be concerned.

For the determination of fluorine, cyclic neutron activation analysis (CNAA) is not only more convenient than the traditional colorimetric, ion-selective electrode, and combustion ion chromatography methods, owing to its character of non-destructive analysis, but also more sensitive than conventional neutron activation methods because CNAA is especially advantageous for determining short-lived nuclides such as ^{20}F ($t_{1/2}$ = 11.03 s), the only isotope of fluorine. The concentrations of fluorine in 20 tea samples including black tea, Pu-erh tea, oolong tea, green tea and flower tea were determined by CNAA under a neutron flux of 9.0×10^{11} $n\cdot cm^{-2}\cdot s^{-1}$ and the conditions of $t_i = t_c = 30$ s, $t_d = t_w = 2$ s, for 6 cycles. The signal of fluorine was measured by a high pure germanium coaxial detector based on 1633 keV γ-peak of ^{20}F from ^{19}F(n, γ)^{20}F reaction. The results indicated that the fluorine content in tea from same tea garden was in the order of black tea > oolong tea > green tea > flower tea. The calefaction process to prevent fresh tea leaves fermentation in green tea manufacture could effectively decrease fluoride in tea leaves. Meanwhile, Shenzhen resident exposure to fluorine from ingestion of tea was assessed.

PO-2-11-31 19214

RADIOTRACER TECHNIQUE: A USEFUL TOOL FOR STUDIES OF THE ENVIRONMENTAL BEHAVIOR OF NANOMATERIALS

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In studies of environment effects of engineered nanomaterials, the detection and quantification of nanomaterials are a special challenge to the researchers. Reliable analytical methods are urgently needed in order to overcome some severe experimental difficulties (e.g. the detection and measurement of nanomaterials in complex environmental or biological samples) associated with this type of research. In this context, radiotracer technique is especially well suited to such studies and have got the chance to demonstrate their enchantment. In comparison with other analytical methods, radiotracer technique has many advantages, such as high sensitivity, good accuracy, and time saving. Moreover, this method can easily distinguish the endogenous and exogenous sources of elements of interest in samples.

In our lab, several radiolabelled nanomaterials, such as ^{125}I-SWNTols, ^{125}I-MWNTols, ^{125}I-$C_{60}(OH)_x$, and nano-$^{59}Fe_2O_3$ have been synthesized and their ADME in mice or rats have been studied. In this presentation, we will report our recent results on radioactive ceria nanoparticles (nano-$^{141}CeO_2$). Nano-^{141}CeO2 with different sizes were synthesized by a precipitation method using $^{141}Ce(NO_3)_3$ as the starting material. Several investigations such as uptake by plants, kinetic behaviour in simulated aquatic ecosystem, pulmonary deposition and translocation in rats, etc. were carried with nano-$^{141}CeO_2$. The following results are obtained: (1) Nano-$^{141}CeO_2$ can be absorbed by plants in size and plant species-dependent manners. (2) There were differences in the distribution, accumulation and transfer dynamics of nano-$^{141}CeO_2$ in different aquatic organisms, *C. demersum* showed a high ability of accumulation of ^{141}nano-CeO_2 from water. (3) The translocation of nano-$^{141}CeO_2$ from the respiratory epithelium towards circulation did occur after the nano-ceria was deposited in the alveolus, but in a quite slow way.

PO-2-12-1 17754

CHARACTERIZATION OF ^{57}Fe IMPLANTED SnO_2 FILMS BY MOSSBAUER SPECTROSCOPY AND NUCLEAR INELASTIC SCATTERING

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The as implanted sample at room temperature and post-annealed samples did not show Kerr effect, but the sample implanted with $1x10^{17}$ Fe ions/cm^2, heated at 300^{o}C, showed a little Kerr effect although the magnetic sextets were not clearly observed in ^{57}Fe CEM spectra. The Kerr effect disappeared after post-annealing. This suggests that the number of magnetic defects decreases by absorption of oxygen [1]. We also showed that the bulk magnetization is enhanced by co-doping of Sb and Fe into SnO_2 powder [2]. We have analyzed the nanostructure of SnO_2 films doped with ^{57}Fe by conversion electron Mossbauer spectroscopy (CEMS) and nuclear inelastic scattering (NIS) at SPring8.

We implanted ^{57}Fe with $5x10^{16}$ ions/cm^2 into SnO_2 films containing 0.1% Sb and 3% Sb at the substrate temperature of 500^{o}C in vacuum. Kerr rotation angles for 0.1% Sb doped SnO_2 film were larger than that for 3%Sb doped SnO_2 films. The samples post-annealed at 400^{o}C for 6 hours also showed the Kerr effect. DCEM spectra were measured by discriminating conversion electrons with a back scattered type of gas counter [3]. As the results, four subspectra were observed: two doublets are assigned to paramagnetic Fe^{3+} and Fe^{2+} species and two broad sextets to site A and site B of magnetite. For 0.1%Sb doped SnO_2 films the relative area of the magnetite phase was larger than for 3%Sb doped SnO_2 films. After post-annealing, two sextets changed into one broad sextet, which is due to fine maghemite. The ferromagnetic behaviors of Fe implanted tin oxide films were attributed mainly due to the formation of magnetite for the as implanted samples and of maghemite for the post-annealed samples, respectively, rather than magnetic defects.

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PO-2-12-2 21905

H/D ISOTOPE EFFECT AND MAGNETIC PROPERTIES OF CYANIDE-BRIDGED Nd(III)-Fe(III) COMPLEX

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During searching for new functional materials acting as photo-controllable molecule-based magnets, we have discovered $Nd(DMF)_4(H_2O)_3Fe(CN)_6 \bullet H_2O$ complex as the first material among 3d-4f cyanide-bridged complexes [1]. However, detailed mechanism have never been elucidated especially based on correlation between crystal structures – electronic states nevertheless of systematic studies on crystal structures [2], metal-substitution [3], and other strategy to design photo-magnetic materials [4]. As one of viewpoints, we focused on flexibility of crystal structures by varying external physical conditions such as temperature.

In order to discuss the role of crystal lattice (intermolecular hydrogen bonds) and/or coordination environment (3d electronic states coupled with 4f ions) separately, we prepared four H/D isotope substituted $Nd(DMF)_4(H_2O)_3Fe(CN)_6 \bullet H_2O$ complexes by employing D_2O and d-DMF. We have measured magnetic properties (MH plots at 0-5T at 5K; MT plots at 5-300K at 0.5 T), ^{57}Fe Mossbauer spectra (at 12, 100, 173, and 300 K), and soft X-ray absorption spectra of $Fe2p_{3/2}$ and $Fe2p_{1/2}$ (variable temperature at 70-300K) at KEK PF BL-19B.

Slow diffusion of aqueous solution (10 mL) of $K_3[Fe(CN)_6]$ (0.1 mmol) onto DMF solution (10 mL) of $Nd(NO_3)_6 \bullet nH_2O$ (0.1 mmol) gave rise to yellow prismatic single crystals of $Nd(DMF)_4(H_2O)_3Fe(CN)_6 \bullet H_2O$ at 298 K [1]. The H/D isotope complexes were prepared by using the corresponding D_2O and d-DMF solvents and characterized appropriately. Little shift of cyanide band of IR spectra suggested that there was no evidence of H/D isotope effects for the cyanide-bridges and superexchange magnetic interaction between Nd(III) and Fe(III) ions. The variable temperature measurements of magnetic properties exhibited that the most largest difference (less than contribution of s=1/2) between the four complexes could be seen for the MT plots at 300 K, which suggested the importance of intermolecular hydrogen bonds in the crystal lattice. Moreover, ^{57}Fe Mossbauer spectra indicated that the four complexes contained low-spin Fe(III) ions at all the temperature range, which suggested that thermally-accessible structural change did not result in changing Fe(III) electronic states.

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PO-2-12-3 17788

POSITRONIUM CHEMISTRY IN NANODROPLETS

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Liquids confined in nano pores–nanodroplets-show unusual properties compared to bulk liquid. This phenomenon has great relevance in fundamental research as well as in applications which is well documented. Positronium atoms offer unique advantages in the study of nanodroplets especially phase transitions [1-2]. In the present work unusual freezing/melting behavior of different organic liquids like benzene, ethylene glycol and isopropanol confined in nanopores of ZSM-5 zeolite and silica gel has been studied using positron annihilation spectroscopy. It is seen that the freezing point of benzene confined in nano pores is decreased from its bulk value, where as the freezing point is elevated in confined ethylene glycol and isopropanol. This variation in freezing points is mainly due to the difference in the interfacial interaction between the pore wall and liquid surface. The interaction of benzene molecules with the pore surface is weakly attractive/repulsive, where as it is highly attractive for ethylene glycol and isopropanol. The phenomenon of shifting in freezing point as a function of nanopore size could not be explained on the basis of classical thermodynamics (Gibbs-Thomson relation). However, the experimental results were better explained by considering the small molecular cluster formation of confined molecules inside the pore. It was observed that the dynamics of phase transition of ethylene glycol and isopropanol in ZSM-5 is quite different from each other. This difference is due to the variation in the interfacial H-bonding of ethylene glycol and isopropanol, with the pore wall. It is to be noted that ethylene glycol has both the intra-and inter-molecular H-bonding, where as isopropanol has only the inter-molecular H-bonding. This makes the interfacial structure of ethylene glycol different from that of isopropanol resulting in different behavior in the phase transition. Results will be discussed in more details.

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PO-2-12-4 20848

IN-BEAM MÖSSBAUER SPRCTROSCOPY OF ^{57}Mn IMPLANTED INTO ALUMINUM OXIDE

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Aluminum oxide (Al_2O_3) has been extensively investigated in material science since its optical property is controllable by the nature and amount of impurity. In spite of the long history of studies there remain unresolved problems and Al_2O_3 still attracts a lot of research interest. One of the topics is the state of the trace amount of transition metal impurity in Al_2O_3, which has been a test field for verification of theoretical calculation (e. g. [1]).

The Al_2O_3:Fe system has been extensively investigated by Mössbauer spectroscopy. One of the reasons of such interest is that the most stable phases of Al_2O_3 and Fe_2O_3 at room temperature have the same crystal structure and the oxides easily form solid solution. Trace impurity studies using ^{57}Fe implantation into Al_2O_3 by absorption Mössbauer spectroscopy observed Fe^{2+} species in addition to substitutional Fe^{3+} [2, 3], however, the implantation energy of the previous works were limited to probe only the surface of the sample material and the aggregation of the implanted iron was suggested. Emission Mössbauer spectroscopy has high sensitivity and the ability to characterize extremely small amount of components in solids. We have reported the studies of ^{57}Mn implanted into $KMnO_4$ and O_2 solids in order to investigate the ^{57}Fe species arising from the β-decay of ^{57}Mn [4, 5]. Direct implantation of ^{57}Mn from a high energy heavy ion accelerator enables the ion buried into the deep bulk of the sample and hence the aggregation of the prove atoms is almost negligible and the defects caused by the implantation are depressed. Recently, we improved the detection system for in-beam ^{57}Mn Mössbauer spectroscopy and succeeded in improving the quality of spectrum dramatically. In this contribution we report the result of the new experimental system applied to the investigation of Fe impurity in Al_2O_3.

The experiment was carried out at HIMAC (Heavy Ion Medical Accelerator in Chiba). The ^{57}Mn beam was produced by the nuclear projectile fragmentation of ^{58Fe} accelerated at 500 MeV per nucleon bombarding to a beryllium target. ^{57}Mn nuclei were implanted into a sample after passing through degraders and stopped in an Al_2O_3 polycrystalline disk (50 mm diameter and 5 mm thickness) purchased from Furuuchi Chemical Co. The 14.4 keV Mössbauer γ-rays emitted from ^{57}Mn were detected by a parallel-plate avalanche counter (PPAC) combined with a plastic scintillation β-veto counter. The Mössbauer spectrum of ^{57}Mn implanted into Al_2O_3 measured at room temperature was relatively simple and was fitted into the combination of a singlet (IS = -0.44 mm/s) and a doublet (IS = -0.72 mm/s, QS = 1.9 mm/s). The singlet peak is assigned to high-spin Fe^{3+} at the substitutional site of Al^{3+} in Al_2O_3 crystal. The doublet might be interstitial Fe^{3+}.

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IN-BEAM MOSSBAUER SPRCTROSCOPY OF ^{57}Mn IMPLANTED INTO MAGNESIUM OXIDE

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A study of ^{57}Fe in-beam Mössbauer spectroscopy using ^{57}Mn provides direct information on exotic state of unstable nuclear probes and on electronic properties of the surrounding materials. We have reported the studies on ^{57}Mn implanted into $KMnO_4$ [1] and O2 solids [2]. Recently, our detection method was successfully improved to obtain in-beam Mössbauer spectra with very large S/N ratio using HIMAC (Heavy Ion Medical Accelerator in Chiba). Here, we demonstrate the validity of this technique applying to a simple metal oxide solid MgO.
The MgO:Fe system prepared by mixing iron oxide and magnesium oxide has been investigated Fe^{3+}
by Mössbauer spectroscopy, in which divalent Fe, vacancy associated , ferrimagnetic magnesioferrite, ferromagnetic bcc iron and antiferromagnetic Fe_2O_3 were observed [3, 4]. Implantation of ^{57}Fe ions into MgO was performed, and many component including Fe^{2+}, Fe^{3+}, and Fe^0 were reported [5]. Direct implantation of ^{57}Mn provides very sensitive nuclear probe and Mössbauer spectra can be obtained using very small amount of probe atoms, and hence the aggregation of the prove atoms is almost negligible and the defects caused by the implantation are depressed.
The ^{57}Mn beam was produced as a nuclear projectile fragment of the ^{58}Fe beam. ^{57}Mn nuclei were implanted into a sample after passing through Pb/Al/acrylic plates in order to stop all the ^{57}Mn nuclei at adequate depth in the sample. The sample used was a MgO polycrystalline disk (50 mm diameter and 5 mm thickness) purchased from Furuuchi Chemical Co. The 14.4 keV γ rays emitted from ^{57}Mn were detected by a parallel-plate avalanche counter (PPAC) with a built-in ^{57}Fe enriched stainless-steel absorber, which was mounted on a Mössbauer transducer to measure the spectra. The Mössbauer spectrum of ^{57}Mn implanted into MgO measured at room temperature was relatively simple, which was fitted into the combination of a singlet (δ = -0.91 mm/s) and a doublet (δ = -0.55 mm/s, ΔEq = 1.3 mm/s). The singlet peak is assigned to high-spin Fe^{2+} surrounded by six O atoms, which substitute Mg^{2+} in MgO crystal. Whereas the assignment of the doublet is difficult; it might be an Fe atom with vacancy of O atoms in neighbor, or an Fe atom in interstitial position of MgO lattice. Density functional calculations using ADF program set [6] applying cluster model were performed to estimate the electronic structure of the Fe atom in MgO lattice in various environment in order to make an assignment of the doublet peaks.

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LASER DEPOSITION OF IRON IN OXYGEN ATMOSPHERE

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Laser deposition is a very useful method to produce films controlling their composition. Laser ablation produces highly energetic atoms (electronic and translational energies), and thus it induces chemical reactions in gas phase. Iron oxide films were produced by laser-deposition of Fe in an oxygen atmosphere. The compositions of the films changed depending on the pressure of the O_2 atmosphere and the temperature of the substrates. In this study, the effects of gas-phase reactions were studied by the laser deposition of Fe in O_2 gas or O_2/Ar gas mixture.

Second harmonics 532 nm of a YAG laser (NewWave, TEMPEST 10, 100 mJ/pulse, 5 ns, 2 Hz) was focused by a convex lens onto an iron metal in a vessel with controlling the pressure of O_2 or O_2/Ar gas mixture. The temperature of the substrate was maintained at the desired temperature (300 or 600 K) using a resistive heater. Mössbauer spectra of the samples at room temperature were measured in a transmission geometry using a ^{57}Co/Rh source. The films were also investigated by X-ray diffraction and scanning electron microscopy.

A film produced by the laser deposition of Fe onto an Al substrate at 300 K in 670 Pa of O_2 atmosphere was constituted of Fe_2O_3 (sextet) and trivalent iron particles (doublet), whereas the film produced in 7 Pa of O_2 atmosphere was constituted of Fe_3O_4 (two sets of sextet), divalent iron oxide particles (doublet), and trivalent iron particles (doublet). Iron oxide particles were produced by the reaction of Fe atoms with oxygen molecules in gas phase, and the following surface reaction and the crystal growth produced Fe_3O_4 films. When the film was produced in O_2/Ar gas mixture (7 Pa / 633 Pa), the Mössbauer spectrum with magnetic hyperfine distribution was observed. The collision of Fe and gas molecules (O_2 or Ar) reduces the energy to grow crystal on the surface, and the obtained film had large numbers of defects. The effects of substrate temperatures while laser deposition was also studied in order see the crystal growth in the deposited films.

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LOCAL FIELDS AT IMPURITY SITES IN ZnO

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Zinc oxide (ZnO) is one of the most promising compounds in wide fields of technology and industry because of its optoelectronic properties applicable to functional devices. It is well known that those intriguing physical properties depend on the type and concentration of impurity ions incorporated in the matrix. In order to study in detail the role of impurities, therefore, it is important to obtain information on the impurity sites. In this study, we doped group 13 elements as impurities in polycrystalline ZnO, and measured the local fields in the vicinity of the dopants by means of the time-differential perturbed angular correlation (TDPAC) method with the probe ^{111}Cd formed in the disintegration of ^{111}In [1, 2].

The TDPAC method is a nuclear spectroscopic technique, which provides atomic level information on a local scale in matter through hyperfine interactions between probe nuclei and the surrounding spins and charge distribution. Because group 13 elements including In are regarded as ideal donors for II-VI compound semiconductors owing to their valence, investigation of the ambient field of the site occupied by ^{111}In(→^{111}Cd) nucleus can thus fulfill the present objective. We here report a drastic difference in the electric field gradient (EFG) values at the ^{111}Cd nuclei between doped ZnO and undoped one. Showing a temperature dependence of the damping trend of the well-defined TDPAC spectra, we discuss microscopic observations unexpected from the result of a bulk experiment on electric conductivity.

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