Combining Analytical Techniques for Trace Elements in Uranium Oxide (U_3O_8)

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SUMMARY. Traditionally XRF is used to analyse the major elements in a solid high purity product and ICP to analyse the trace elements in the dissolved solid; hence different sample preparation techniques are required. Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) as a technique can be used in parallel with X-ray Fluorescence (XRF) with the same analytical methodology. Trace elements present in U_3O_8 are investigated using LA-ICP-MS as these are below detection limits of XRF instruments. A certified reference material and an in-house processed yellow cake were investigated using the two techniques.

1. INTRODUCTION.

Trace impurity concentrations in uranium materials are an important quality control parameter in the production of high-purity uranium metals of uranium oxides. Certain impurities can alter the physical characteristics of the high purity material and the neutron absorption characteristics of light impurity elements can attenuate nuclear processes in the material. This becomes very important when fuel for nuclear reactor is produced. A fast and accurate analytical method is essential for trace impurities, as exposure to the analyst must be kept to the minimum Crain *et al* (1).

LA-ICP-MS, is a vaporisation process in which a laser is used as the primary energy source. When a laser beam of sufficient power density strikes a solid material, it generates particle aerosols into the gas phase. This ablation process is caused by the interaction of laser photons with the solid material. Typically, a solid sample is placed inside an ablation-sampling cell, and a laser beam with an aid of a microscope is focused onto the surface of the sample. When the laser is fired, a cloud of particles are produced. These particles are removed from the sampling cell by an argon or helium carrier gas, and are swept into the ICP-MS for analysis. ICP-MS is capable of providing a high throughput of samples while analysing at levels as low as parts per trillion (ppt). The elements in the sample are ionised in the high temperature argon plasma and then separated on the basis of their mass to charge ratio (m/z). Various sample introduction systems can be linked to the ICP-MS, including laser ablation, depending on what the sample matrix and concentration requires.

The development of LA-ICP-MS was as a result of demands for high throughput and flexibility to measure both liquids and solids. It was most beneficial to combine lasers with emission or mass spectrometer, as it was capable of measuring trace levels in a solid. LA-ICP-MS was first used in 1985 and has found a niche as an important analytical tool since the early 1990s. Most of developmental work for LA-ICP-MS was driven by geologists and mineralogists as a result of their desire for trace analysis of materials such as calcite, glass, quartz and fluorite. What makes LA-ICP-MS such a powerful and flexible sample introduction tool? There is no requirement for sample dissolution and the technique can be used quantitatively if suitable standards are available. The introduction of a dry aerosol (from ablating the solids) as opposed to a wet aerosol reduces the number of polyatomic interferences produced by the sample interacting with water and acid in the plasma. The system is simple to use and is robust for routine operations. LA-ICP-MS is generally used for the analysis of solid samples and has also been very useful for measuring a large number of elements in many minerals at very low levels.

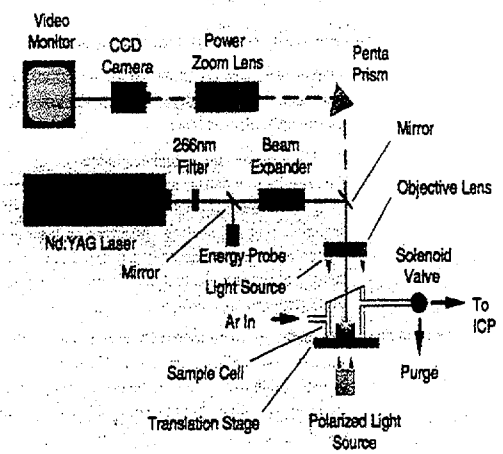

Figure 1 Schematic of a typical Laser Ablation System

XRF utilises the band of continuous radiation produced by the X-ray tube. It is used to determine the elements present in a sample by studying the secondary fluorescent X-ray spectrum produced by the irradiated sample. It provides a high throughput of samples and is a non-destructive method. The samples are unchanged by the testing. It can be used to analyse all elements from atomic weight 5 (Boron) upwards with the exception of Nitrogen. At ANSTO, our instrument is capable of analysing from Fluorine (F) upwards. The measurement can detect elements of concentrations down to 0.2 and 10 parts per million (ppm) with lighter elements such as F being in the 100's of ppm. If the sample for XRF is extracted from a bulk material, the sample must be representative of the material as a whole. As X-ray spectroscopy is a comparative method of analysis, the instrument is first calibrated using standard reference materials. The use of Lithium metaborate and Lithium tetraborate flux fusion was a major breakthrough for XRF sample preparation. Most geological samples are effectively digested by these fluxes to form homogenous glass. This is where LA-ICP-MS and XRF can be used in parallel as the same analytical methodology can be used.

2. EXPERIMENTAL

Trace elements in U_3O_8 were examined using LA-ICP-MS as these were below detection limit of XRF. The major elements were analysed using XRF. The technique was investigated using CUP-2, which is a uranium ore concentrate certified material produced as a joint effort between Canadian Certified Reference Materials Project (CCRMP) and the Analytical Subcommittee of the Canadian Uranium Producers Metallurgical Committee. The test sample used was yellow cake processed by the Cleaner Technology for Uranium Mining and Milling project within the Environment Division. The LA-ICP-MS work was carried out at Macquarie University's GEMOC Key Centre. The laser used was a continuum Surelite I-20 Q-switched Nd: YAG laser with a fundamental infrared (IR) wavelength of 1064 nm. Two frequency doubling crystals provide second and fourth harmonics in the visible at 532 nm and ultraviolet at 266 nm. The 266-nm wavelength provides better coupling and can be focused to a smaller diameter spot for ablation. This is the wavelength that was used for our analysis. As the beam that emerges from the laser is a mixture of IR, VIS and UV it is directed onto a pair of dichroic mirror which reflect the UV and allow the VIS and IR wavelengths to pass through to an beam trap. The laser produced a maximum of about 25 mJ per pulse. Our samples were carried out using 0.3 mJ per pulse. Ablation was monitored in real time using transmitted light and a video camera. The sample is contained within a chamber that is placed on the microscopic stage, and through which the ICP-MS nebuliser gas flows during ablation. The sample remains at atmospheric pressure and this is an advantage over many other analytical techniques where the sample must be under vacuum to permit analysis. As air must not enter the ICP, an arrangement for cell purging to atmosphere is part of the laser ablation system. This is achieved by using a three-way valve in the cell to ICP transport line. The outlet from the sample chamber is connected to a Perkin-Elmer Sciex ELAN 5100 ICP-MS torch by ~1m of 6.4 mm OD x 4.0 mm ID tubing. A 30-mL chamber is installed between the sample chamber and the ICP-MS torch to integrate the ablated material and to suppress spikes that occasionally occur in the signals of some elements during initial stages of ablation. Higher nebuliser flow rates and RF power settings are used for laser ablation compared to solution work to increase sensitivity.

3. RESULTS AND DISCUSSION

Scanning Electron Microscope images of the ablation pits were taken. Absorption of the laser energy in the surface layer is the key to controlled ablation (Fig. 2). It can be seen that some material was redeposited at the edge of the pit. Laser energy and the coupling efficiency with the ablating material will determine the pit created. Optimisation of all conditions will enable clean and regular pits to be acquired.

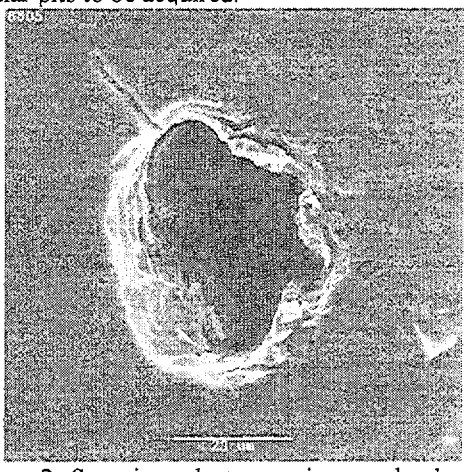

Figure 2 Scanning electron micrograph showing controlled ablation

Catastrophic ablation is when there is uncontrolled spalling of large mineral fragments or entire grains (Fig. 3) Jackson (2). This micrograph shows poor coupling between the laser photons and the glass. In this study 13 elements were investigated and the results showed that there was possibility of elemental fractionation. The dynamic nature of fractionation might be explained by changing efficiency of ionisation of particles due to a

progressively changing particle size during a multiple shot ablation Günther *et al* (3). The entire analysis carried out for this used depth profile. A wide array of procedures has been developed to combat laser-induced elemental fractionation. These include '"raster" sampling, "active focussing" ie raising the sample at the same rate as the laser penetrates into the sample Hirata *et al* (4). "Soft ablation" can also be looked at whereby the incident energy is increased during ablation to maintain constant signal Hirata (5). Bolshov *et al* (6) used short pulse lasers and Norman *et al* (7) suggested low repetition rate ablation. Various mathematical correction procedures are also available Horn *et al* (8). The use of a "jet cell" and matrix matching has also been explored Jackson *et al (9),* Gutierrez-Alonso *et al* (10) and Ketchum *et al* (11).

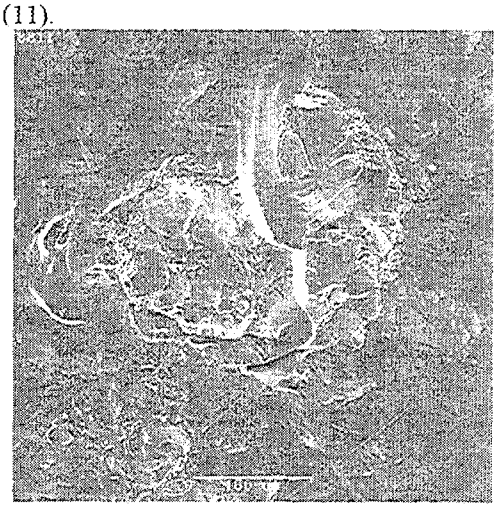

Figure 2 Scanning electron micrograph showing catastrophic ablation

Element	Certified Value mg/kg	LA-ICP-MS mg/kg	XRF mg/kg
U	754200		790000
Ca	6200	6480	8000
Fe	3110	3010	4000
K	1100	1020	
Mg	2290	2210	2000
Mo	690	660	
Na	4590	4480	
Ni	29	30	
Si	1700	2160	
Ti	190	195	200
V	660	660	700
Zr	440	500	

As can be seen from the results, not all elements are close to the certified values. This can be explained in terms of elemental fractionation and poor coupling. In future studies, rastering and active focussing will be investigated.

The test sample used was a uranium concentrate obtained from the Cleaner Technology Project. It was possible to obtain results for elements that were undetectable by the XRF. Table 2 shows some of the trace elements present in the test sample.

Element	LA-ICP-MS mg/kg	XRF mg/kg
U		827000
Ca	27	ND
Fe	45	ND
K	NP	NP
Mg	37	ND
Mo	NP	NP
Na	14	ND
Ni	NP	NP
Si	168	200
Ti	NP	NP
V	NP	NP
Zr	NP	NP

ND denotes that element wasn't below detection limit.
NP denotes element not present.
More elements were detected using then LA-ICP-MS, as these were below the detection limits of the XRF.

4. CONCLUSION

Trace elements in U_3O_8 can be measured accurately using LA-ICP-MS. XRF was found to be the best for the major component, which in this case was uranium. However, to obtain isotopic ratio an MS technique would be more useful. The lithium-borate fusion glass used for XRF can be made rapidly with a high degree of homogeneity. The advantage of combining LA-ICP-MS and XRF is that there is no additional sample preparation. Radioactive materials are easier to handle as the hazards are lower when they are dissolved in glass. It is easier to handle waste as it is already in a solid form. Further investigations are needed to perfect this technique for trace element analysis. The work carried out at ANSTO so far on LA-ICP-MS is at a developmental stage. We are in the process of gathering knowledge and expertise in this area and see more opportunities arising in the future for high quality analytical work.

5. ACKNOWLEDGMENTS

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