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EVALUATION OF NEUTRON ACTIVATION ANALYSIS FOR THE MEASUREMENT OF ISOTOPIC ABUNDANCES IN MOLYBDENUM-98 ENRICHED MOLYBDENUM

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ABSTRACT

Molybdenum enriched to approximately 50 per cent ^{98}Mo is required for the development of a portable ^{99m}Tc generator based on the zirconium molybdate gel system developed by the AAEC. It has been proposed that existing AAEC facilities be used to enrich molybdenum, and neutron activation analysis has been evaluated as a means of monitoring the enrichment process.

Simulated enriched targets of MoO_3 with ^{98}Mo abundances ranging from 30 to 90 per cent were prepared by diluting 96.87 per cent enriched $^{98}MoO_3$ with the natural trioxide. These targets were each irradiated simultaneously with a reference natural MoO_3 target in a thermal neutron flux of 7.5×10^{12} neutrons $cm^{-2}s^{-1}$ where the reactions $^{92}Mo(n,\gamma)\ ^{93}Mo$, $^{98}Mo(n,\gamma)\ ^{99}Mo$ and $^{100}Mo(n,\gamma)^{101}Mo$-$^{101}Tc$ occur. The isotopic abundances of ^{98}Mo and ^{100}Mo were determined with an accuracy ± 2 per cent by comparing the yields of ^{99}Mo-^{99m}Tc and ^{101}Mo-^{101}Tc, respectively, in the enriched and natural targets. The activation yield of ^{93}Mo was too low for the determination of the ^{92}Mo abundances.

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ACCURACY; EXPERIMENTAL DATA; GAMMA RADIATION; ISOTOPE RATIO; ISOTOPE SEPARATION; MOLYBDENUM OXIDES; MOLYBDENUM 98; MOLYBDENUM 98 TARGET; MOLYBDENUM 100; MOLYBDENUM 100 TARGET; MOLYBDENUM 92; NEUTRON ACTIVATION ANALYSIS; NEUTRON FLUX; NEUTRON REACTIONS; RADIOISOTOPE GENERATORS; TECHNETIUM 99;

CONTENTS

1. INTRODUCTION

The specific activity of ^{99}Mo produced by the (n,γ) reaction in the AAEC's materials testing reactor HIFAR, which has a thermal neutron flux of approximately 7.5×10^{13} neutrons cm^{-2} s^{-1} with an epithermal flux index of 0.119 [Connolly *et al.* 1968], is of the order of 2 Ci per gram of molybdenum. To exploit fully the potential of the AAEC's zirconium molybdate gel generator system [Evans *et al.* 1982], higher specific activity (n,γ) ^{99}Mo is desirable. Without an increase in neutron flux, the specific activity can only be increased by using target material enriched in ^{98}Mo. The natural isotopic abundance of ^{98}Mo is 24.4 per cent. The possibility of adapting existing facilities at the AAEC Research Establishment, to allow enrichment of ^{98}Mo to an abundance of 50 per cent or better, is being investigated.

To supplement established techniques such as mass spectrometry, neutron activation analysis (NAA) has been proposed for measuring the post-enrichment isotopic abundances of the molybdenum isotopes, particularly that of ^{98}Mo.

2. ACTIVATION OF STABLE MOLYBDENUM ISOTOPES

The stable isotopes of molybdenum and their abundances are given in **table 1**. Three of the isotopes, ^{92}Mo, ^{98}Mo and ^{100}Mo, yield radioactive products as a result of (n,γ) reactions. The activation and decay products are shown in **figure 1**. Depending on the activation yields, these reactions could be used to determine the isotopic abundances of the three stable isotopes.

The abundances in enriched materials can be determined from the simultaneous activation of natural and enriched samples followed by a comparison of the activity in the two targets using gamma spectrometry. The principal gamma peaks of the activation products, ^{99}Mo, ^{99}Mo-^{99m}Tc, ^{101}Mo, and ^{101}Tc, are given in **tables 2-5**, respectively.

3. SIMULATION OF ENRICHED MOLYBDENUM

To cover the possible range of enriched products, targets with nominal ^{98}Mo abundances between 30 and 90 per cent were prepared by mixing molybdenum trioxide (MoO_3) with a 96.8 per cent ^{98}Mo enrichment with the natural trioxide in the appropriate proportions. The enriched MoO_3 was obtained from Oak Ridge National Laboratory (ORNL) and the isotopic and spectrographic analyses are given in **table 6**. The natural MoO_3 was of analytical grade and purified for use as target material for ^{99}Mo production [Lee *et al.* 1985]. A nominal target mass of 10 mg was used for assessment. Two 100 mg samples with nominal enrichments of 30 and 50 per cent, respectively, were also examined to evaluate the effect of sample mass on measurement accuracy.

The masses of enriched and natural oxide required for a given abundance in the mixture were calculated from the abundances in each component, the atomic weights of the molybdenum isotopes and the oxide molecular weights. After weighing, the actual abundances in each sample were recalculated for all the natural molybdenum isotopes (**table 7**). The method of calculation is described in **appendix A**. Weighing accuracy was limited by the balance available and the accuracy of the abundances was estimated to be of the order of ±2 per cent.

4. ACTIVATION ANALYSIS

Each simulated enriched target was analysed by comparison with a natural MoO_3 reference sample after irradiation in a nominal thermal neutron flux of 7.5×10^{12} neutrons cm^{-2} s^{-1}. The samples were contained in separate polythene pill packs in an outer irradiation can. Separate irradiations of each pair of targets were required to determine the ^{92}Mo, ^{98}Mo and ^{100}Mo abundances because of their levels of activity and different half-lives. A gamma spectrometer with a pure germanium detector was used to analyse the irradiated targets. The source-detector distance was 15 cm.

Enrichments were calculated from the ratios of the photo peak areas for the enriched and natural targets. As this comparative method eliminates the need for activation calculations, it is independent of the actual neutron flux, the effective activation cross section and the detector efficiency.

4.1 Molybdenum-98 Measurements

Each target pair was irradiated for one hour (10 mg targets) or fifteen minutes (100 mg targets) and allowed to decay for five hours before counting to determine the peak area ratios. It was impractical to use shorter decay times to allow the same irradiations to be used for determination of ^{100}Mo from the ^{101}Mo- ^{101}Tc peaks.

The analysis was based on the 0.140, 0.180, 0.739 and 0.771 MeV peaks of ^{99}Mo-^{99m}Tc. The enriched and natural targets were counted alternately for five minutes. This procedure was repeated up to five times. Each pair of counts was corrected for decay to a fixed time, then the ratios of the peak heights were calculated. The counts for the 0.140 MeV peak were corrected for ^{99m}Tc growth to the reference time. The results are summarised in **table 8**. The isotopic abundances in the simulated enriched target were calculated from the peak ratios, as shown in **appendix B**. The calculation for target No. 2 is given as an example.

4.2 Molybdenum-100 Measurements

Each target pair was irradiated for 10 minutes (10 mg targets) or two minutes (100 mg targets) and the first count commenced within 15 minutes of removal from the reactor. The analysis was based on the 0.192, 0.506, 0.591 and 1.012 MeV peaks of ^{101}Mo and the 0.306 MeV peak of ^{101}Tc. The enriched and natural targets were counted alternately for five minutes, with an interval of two minutes between each count to allow data readout and sample change. This procedure was repeated until each sample pair had been counted five times.

Each pair of counts was corrected for decay to a fixed time, then the ratios were calculated. The counts for the ^{101}Tc at 0.306 MeV were corrected to the reference time using the standard growth equations for a parent-daughter system. The relatively higher count rate for this peak suggested that it would give the most accurate ratio. However, the uncertainties in making the decay-growth corrections for the short half-lives involved meant that the accuracy was similar to that of the other ratios. The method for calculating the isotopic abundances is given in **appendix B**. The results are summarised in **table 9**.

4.3 Molybdenum-92 Measurements

The half-life of ^{93}Mo suggested that an irradiation for several hours, followed by a similar decay period to eliminate interfering ^{101}Mo-^{101}Tc peaks, would be required for ^{92}Mo determination using the 0.263 and 0.684 MeV peaks. In practice, the resulting peak areas were too small for the ratios to be calculated owing to the low activation cross section of ^{92}Mo. Thus, it was not feasible to determine ^{92}Mo by the simple activation analysis technique described here. More advanced techniques were not investigated.

5. ACCURACY

It was estimated that the overall accuracy of the enrichment measurement was of the order of ± 4 per cent. The principal factors affecting the accuracy were the errors in the target masses and photo-peak ratios. The targets were prepared using a balance accurate to only ± 0.1 mg. A weighing accuracy of better than ± 0.1 per cent is required if the method is to be used to determine isotopic abundances from an actual enrichment process. For both ^{98}Mo and ^{100}Mo determinations, the accuracy of the peak ratios was ± 2 per cent. In practice, it would be possible to select count times and post-irradiation decay times to achieve an accuracy of ± 0.5 per cent for the peak ratios. The accuracy of the measured isotopic abundances would then be reduced to about ± 1 per cent.

6. CONCLUSIONS

This investigation has shown that activation analysis can be used to measure ^{98}Mo and ^{100}Mo isotopic abundances in enriched molybdenum with an accuracy of the order of ± 2 per cent. The analysed samples must be in a stable chemical form, such as the metal or its trioxide, suitable for reactor irradiation. The enriched and natural reference targets must be in the same chemical form.

7. REFERENCES

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Evans, J.V., Moore, P.W., Shying, M.E., Sodeau, J.M. [1982] - A new generator for technetium-99m. *Proc. 3rd World Congress on Nuclear Medicine and Biology*, 2: 1592.

Lee, E.J., Sorby, P.J., Barnes, R.K., Boyd, R.E. [1985] - Development of a pilot plant for the removal of rhenium from molybdenum trioxide. AAEC/E615.

TABLE 1
THE STABLE ISOTOPES OF MOLYBDENUM AND THE RADIOACTIVE PRODUCTS OF (n,γ) ACTIVATION

Stable Isotopes	Abundance Atom (%)	Radioactive Product and Half-life	Daughter Product and Half-life
^{92}Mo	14.8	^{93m}Mo (6.9 h)	^{93}Mo (3000 y)
^{94}Mo	9.1	-	-
^{95}Mo	15.9	-	-
^{96}Mo	16.7	-	-
^{97}Mo	9.5	-	-
^{98}Mo	24.4	^{99}Mo (66.02 h)	^{99m}Tc (6.02 h)
^{100}Mo	9.6	^{101}Mo (14.6 m)	^{101}Tc (14.2 m)

TABLE 2
PRINCIPAL GAMMA PEAKS AND ABUNDANCES FOR ^{93}Mo

Photon Energy (MeV)	Abundance (%)
0.1139	0.71
0.263	61.2
0.684	91.9
0.948	0.2
1.363	0.62
1.477	99.4
2.162	0.08

TABLE 3
PRINCIPAL GAMMA PEAKS AND ABUNDANCES FOR ^{98}Mo - ^{99m}Tc

Photon Energy (MeV)	Abundance (%)
0.140	90.3
0.181	6.06
0.366	1.193
0.739	12.194
0.777	4.32
0.823	0.133

TABLE 4
PRINCIPAL GAMMA PEAKS AND ABUNDANCES FOR ^{101}Mo

Photon Energy (MeV)	Abundance (%)
0.192	25.0
0.196	2.0
0.334	7.0
0.398	2.0
0.506	15.0
0.591	20.0
0.695	11.0
0.871	1.0
1.012	25.0
1.533	11.0
1.674	3.0

TABLE 5
PRINCIPAL GAMMA PEAKS AND ABUNDANCES FOR ^{101}Tc

Photon Energy (MeV)	Abundance (%)
0.127	2.35
0.179	0.56
0.183	1.55
0.306	91.0
0.531	1.03
0.715	0.64
0.929	0.82

TABLE 6
ISOTOPIC AND SPECTROGRAPHIC ANALYSES OF ENRICHED MoO_3

Element: Molybdenum Series: PK
Isotope: ^{98}Mo Sample: 187905

Isotopic Analysis			Spectrographic Analysis	
Isotope	Atom %	Precision	Element	%
92	0.37	0.01	Ag <0.01	Mn <0.02
94	0.26	0.01	Al <0.05	Mo M*
95	0.52	0.01	B <0.01	Na <0.01
96	0.66	0.01	Ba <0.01	Nb <0.05
97	0.70	0.01	Be <0.001	Ni <0.02
98	96.87	0.06	Bi <0.02	Pb <0.02
100	0.62	0.01	Ca <0.01	Pt <0.05
			Cd <0.05	Rb <0.05
			Co <0.05	Sb <0.05
			Cr <0.05	Si <0.01
			Cs <0.05	Sn <0.02
			Cu <0.01	Sr <0.01
			Fe <0.02	Ta <0.05
			Ga <0.05	Ti <0.01
			Ge <0.05	V <0.02
			Hg <0.05	W <0.05
			K <0.01	Zn <0.2
			Li <0.005	Zr <0.05
			Mg <0.01	

* M = major element

TABLE 7
ISOTOPE ABUNDANCES OF MOLYBDENUM ISOTOPES IN SIMULATED ENRICHED TARGETS PREPARED BY MIXING NATURAL (NAT) AND ORNL ENRICHED (ENR) MoO_3. THE MASSES OF MOLYBDENUM FROM THE NATURAL AND ENRICHED COMPONENTS ARE GIVEN.

Target No	Mass Mo in Target (mg)		Isotopic Abundances in "Enriched" Target (%)						
			Nuclide						
	Nat	Enr	92	94	95	96	97	98	100
1	0.000	6.709	0.37	0.26	0.52	0.66	0.70	96.87	0.62
2	0.719	5.971	1.90	1.20	2.20	2.40	1.70	88.90	1.60
3	1.959	5.179	4.40	2.70	4.80	5.10	3.10	76.70	3.10
4	2.359	4.126	5.70	3.50	6.20	6.60	3.90	70.10	3.90
5	3.399	3.522	7.50	4.60	8.10	8.60	5.10	60.90	5.10
6	4.252	2.294	9.80	6.00	10.60	11.20	6.50	49.40	6.50
7	6.645	1.516	12.20	7.50	13.10	13.70	7.90	37.60	8.00
8	5.998	0.443	13.80	8.50	14.90	15.60	8.90	29.30	9.00
9	62.451	4.696	13.80	8.50	14.90	15.60	8.90	29.30	9.00
10	44.595	23.427	9.90	6.10	10.70	11.20	6.50	49.00	6.50

TABLE 8
MEASURED ^{98}Mo ISOTOPIC ABUNDANCES IN THE SIMULATED ENRICHED TARGETS

Target No	Calculated ^{98}Mo Abund.(%)	Photo Peak Ratio	M_n[(a)] (mg)	E + N[(b)]	Experimental Mo Abund.(%)
1	96.87	3.96	6.71	0.0686	98.5
2	88.9	3.73	6.29	0.0685	87.8
3	76.7	3.48	6.59	0.0733	79.5
4	70.1	2.83	6.60	0.0667	71.2
5	60.9	2.50	6.67	0.0714	59.4
6	49.4	1.96	6.57	0.0677	48.4
7	37.6	1.89	6.52	0.0848	37.0
8	29.2	1.13	6.50	0.0670	27.9
9	29.4	1.20	66.99	0.6989	29.3
10	49.0	1.96	66.65	0.7042	47.3

(a) M_n is the mass of molybdenum in the natural MoO_3 irradiation reference target.

(b) See **appendix A.**

TABLE 9
MEASURED ^{100}Mo ISOTOPIC ABUNDANCES IN THE SIMULATED ENRICHED TARGETS

Target No	Calculated ^{100}Mo Abund.(%)	Photo Peak Ratio	M_n (Mg)	E + N	Experimental ^{100}Mo Abund.(%)
1	0.62	^{100}Mo abundance not measured			
2	1.6	0.180	6.29	0.0685	1.6
3	3.1	0.361	6.59	0.0733	3.2
4	3.9	0.446	6.60	0.0667	4.4
5	5.1	0.574	6.67	0.0714	5.4
6	6.5	0.640	6.57	0.0677	6.2
7	8.0	1.029	6.52	0.0848	7.9
8	9.0	0.931	6.50	0.0670	9.0
9	9.0	0.935	66.99	0.6989	8.9
10	6.5	0.693	66.65	0.7042	6.5

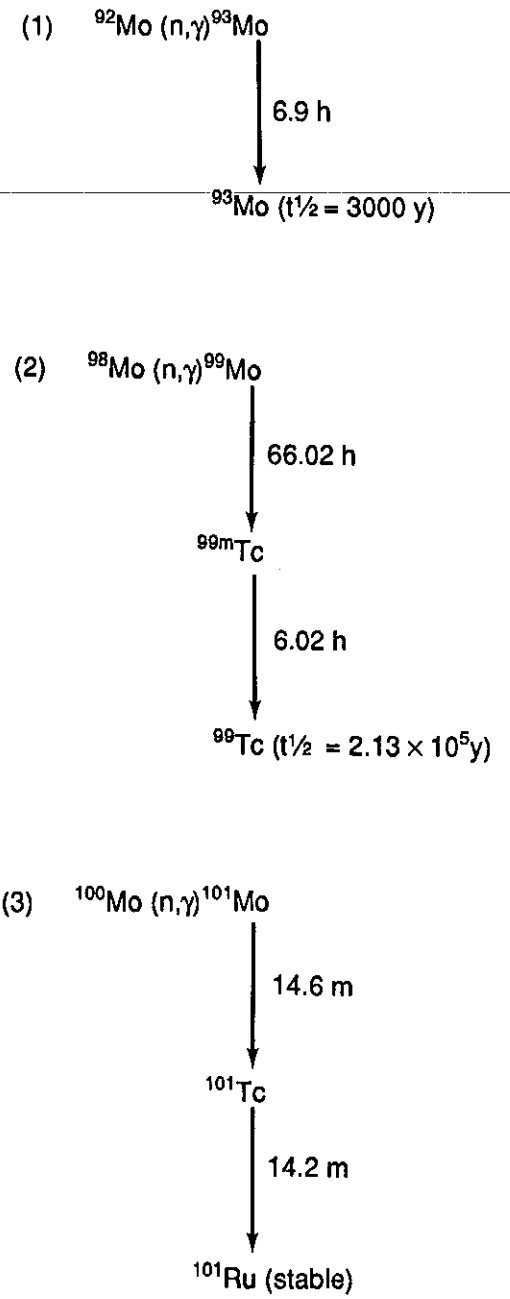

Figure 1. Activation and decay chains for the neutron capture (n,γ) reactions on molybdenum leading to radioactive product isotopes.

APPENDIX A

CALCULATION OF ISOTOPIC ABUNDANCES IN A SIMULATED ENRICHED TARGET: TARGET NO 2 COMPOSITION DATA (see table 7)

MoO_3	Mass (mg)	Mo / MoO_3	Mo	Mass (mg)
Enriched	8.9	0.6709	Enriched	5.97
Natural	1.08	0.6665	Natural	0.72

Mean atomic weight of ORNL enriched Mo 97.85
Mean atomic weight of natural Mo 95.94

In the following calculations below the constant factor of Avogadro's number has been omitted. Numbers of atoms are therefore expressed in relative terms:

$$\text{Relative number of atoms} = \frac{\text{Mass}}{\text{Atomic Weight}}$$

$$\text{For enriched component - relative number of atoms E} = \frac{5.97}{97.85} = 0.061$$

$$\text{For natural component - relative number of atoms N} = \frac{0.72}{95.94} = 0.0075$$

For each isotope in the combined target, the number of atoms in relative terms will be given by

E × isotopic abundance in enriched component +
N × isotopic abundance in natural component.

The calculation is summarised below:

Nuclide	Enriched MoO_3 Abundance (%)	Enriched MoO_3 Contribution (Abund. x E)	Natural MoO_3 Abundance (%)	Natural MoO_3 Contribution (Abund. x N)	Sum of of Contributions	Target Abundance (%)
92	0.37	0.0226	14.8	0.111	0.1336	1.9
94	0.26	0.0159	9.1	0.0683	0.0842	1.2
95	0.52	0.0317	15.9	0.1193	0.1510	2.2
96	0.66	0.0403	16.7	0.1252	0.1655	2.4
97	0.7	0.0427	9.5	0.0713	0.1140	1.7
98	96.87	5.9091	24.4	0.183	6.0921	88.9
100	0.62	0.0378	9.6	0.072	0.1098	1.6

APPENDIX B
CALCULATION OF ISOTOPIC ABUNDANCES FROM PEAK RATIOS

B1 MOLYBDENUM-98

The ^{99}Mo activity present in an irradiated target is proportional to the number of ^{99}Mo target atoms. Hence the ratio of the photopeak areas is also the ratio of the number of ^{98}Mo atoms in the enriched target to the number in the reference natural target.

For any molybdenum target:

$$\text{Number of atoms } ^{98}\text{Mo} = \frac{\text{mass Mo} \times N_A \times \text{isotopic abundance}}{\text{target atomic weight}} \quad ;$$

for the natural reference target:

$$\text{Number of atoms } ^{98}\text{Mo} = \frac{M_n \times N_A \times 0.244}{95.94} \quad ;$$

for the enriched target:

$$\text{Number of atoms } ^{98}\text{Mo} = \frac{M_e \times N_A \times f}{A_e} \quad ;$$

where M_n is the mass of ^{98}Mo in natural target, N_A is Avogadro's number, M_e is the mass of ^{98}Mo in enriched target, f is the ^{98}Mo isotopic abundance in enriched target, and A_e is the mean atomic weight for the enriched target.

In determining the isotopic abundance of a sample produced in an enrichment process, A_e will not be known but may be estimated to better than 0.1 per cent from the expected enrichment. In this experiment, however, it may be shown that

$$\frac{M_e}{A_e} = (E+N) \quad ,$$

where E and N are the relative atom numbers for the target as determined in **appendix A**.

For the enriched target:

$$\text{Number of atoms } ^{98}\text{Mo} = (E + N)\, N_A\, f$$

$$\text{and} \quad \frac{\text{atoms } ^{98}\text{Mo in enriched target}}{\text{atoms } ^{98}\text{Mo in natural target}} = \frac{95.94(E + N)\, f}{M_n \times 0.244}$$

$$= 393.196\, \frac{(E + N)\, f}{M_n} \quad ,$$

but the ratio of the atom numbers is equal to the ratio of the photopeak areas for the two targets (R_{98}), therefore the isotopic abundance of ^{98}Mo in the simulated enriched target is given by

$$f = \frac{M_n \times R_{98}}{393.196\,(E + N)}$$

B1.1 Molybdenum-98 Calculation for Target No 2

Mass of ^{98}Mo in natural reference target M_n = 6.29 mg

Experimental ^{98}Mo photopeak ratio (mean) R_{98} = 3.76

$E + N$ = 0.0685

$$f = \frac{6.29 \times 3.73 \times 100}{393.196 \times 0.0685}$$

^{98}Mo isotopic abundance in target 2 = 87.13%

B2 MOLYBDENUM-100

Using the reasoning given above,

$$\frac{\text{Atoms}^{100}\text{Mo in enriched target}}{\text{Atoms}^{100}\text{Mo in natural target}} = \frac{95.94(E+N)\,f}{M_n \times 0.096} \quad ,$$

where 0.096 is the natural abundance of ^{100}Mo.

If R_{100} is the experimental photopeak ratio for ^{100}Mo, then

$$f = \frac{M_n R_{100}}{999.375(E+N)} \quad .$$

B2.1 Molybdenum-100 Calculation for Target No 2

Mass of Mo in natural reference target = 6.29 mg .

Experimental ^{100}Mo photopeak ratio R_{100k} = 0.180 .

$$E + N = 0.0685 .$$

$$f = \frac{6.29 \times 0.180 \times 100}{999.375 \times 0.0685}$$

^{100}Mo isotopic abundance in target 2 = 1.65% .