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DETERMINATION OF URANIUM FISSION PRODUCT INTERFERENCE FACTOR FOR MOLYBDENUM QUANTIFICATION BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Instrumental Neutron Activation Analysis (INAA) is a technique that provides high precision and accuracy results for the concentration determinations of several elements in different kinds of matrices. However, if the sample contains high uranium concentration in their composition, INAA can provide inaccurate results due to uranium fission product interferences. The molybdenum is one of these elements that suffers interference by uranium fission product, because the ^{99}Mo radioisotope formed by ^{98}Mo neutron capture, used in INAA, is the same that formed in the uranium fission. This kind of interference can be solved by separation of uranium before irradiation or by determining the uranium interference factor to the radioisotope of interest and applying the correction. The present study aims at the following: (1) determination of the Mo interference factor (F_{Exp}^{Mo}) due to the uranium fission product ^{99}Mo by irradiating standards of Mo and U with known masses of these elements (experimental interference factor); (2) determination of the theoretical F_{Th}^{Mo}, in this case it was necessary to determine the epithermal to thermal neutron flux ratio and use the reported nuclear parameters; (3) comparison of the results of the interference factor obtained with values reported in the literature. The interference factor for Mo analysis was obtained in a position 14b shelf 3 of the IEA-R1 nuclear research reactor.

1. INTRODUCTION

Instrumental Neutron Activation Analysis (INAA) is widely used to determine the concentrations of several elements in biological, geological and environment matrices. However, if uranium-rich samples are analyzed, some elements concentration measurements can be hindered due to ^{235}U fission products interferences. Among these elements one that presents strong interference is Mo.

The determination of Mo by INAA is one of the cases that requires attention because Mo and U are found together in a very large number of biological and geological samples [1]. Moreover, in biological studies the determination of Mo with high precision and accuracy is necessary because Mo is an element essential for all forms of life and it may be toxic in higher concentrations [2]. Besides, the determination of Mo with high accuracy in geological matrices is also required in petrogenetic study of rocks formation [1].

The quantification of Mo by INAA is carried out by the ^{98}Mo neutron capture. The product of this reaction, the ^{99}Mo, is also formed in the uranium fission process. Thus, if this interference is not considered by the analyst, the obtained results may have serious systematic errors. The magnitude of the error will depend on the uranium fission yield for the ^{99}Mo production and the U to Mo concentration ratio present in the sample.

The correction of this interference can be solved by making the separation of uranium before sample irradiation which is a hard process or by using the uranium fission interference factor to be applied in the correction of the obtained results, here called apparent concentration. The relation used to make this correction is:

$$[X]_{true} = [X]_{app} - F \cdot [U] \quad (1)$$

Where $[X]_{true}$, $[X]_{app}$, F and $[U]$ are the real Mo concentration, the apparent Mo concentration, the interference factor due to uranium fission and the uranium concentration, respectively. As can be seen in equation 1, the correction magnitude is directly proportional to the interference factor (F) and to the concentration of uranium.

Many authors have published values of uranium fission interference factor for ^{99}Mo [1-7]. The experimental values obtained by these authors have presented a wide range from 1.04 [4] to 2.70 [1]. These spread values are due to the strong dependence on the epithermal to thermal neutron flux ratio (ϕ_{epi}/ϕ_{th}), which varies with the facilities reactor and with the position of the irradiation in the reactor.

In the present study, the determination of uranium fission interference factor for ^{99}Mo was carried out both theoretically, using nuclear parameters reported in literatures and epithermal to thermal neutron fluxes ratio, and experimentally by irradiating synthetic standards of Mo and U.

2. CALCULATION OF URANIUM FISSION INTERFERENCE FACTOR

The uranium fission interference factor for ^{99}Mo is defined as the ratio of the specific activity of ^{99}Mo formed by uranium fission to the specific activity of ^{99}Mo formed by neutron capture of ^{98}Mo, as can be seen in equation 2:

$$F_{Ex}^{Mo} = \frac{m_{Mo}}{m_U} \cdot \frac{A_U^{Mo}}{A_{Mo}} \quad (2)$$

Where m_{Mo} and m_U are the masses of Mo and U, respectively; A_U^{Mo} and A_{Mo} are the activities of ^{99}Mo formed by uranium fission and originated by neutron capture of ^{98}Mo, respectively.

The value obtained by the equation 2 is called *experimental interference factor*. The determination of uranium fission interference factor by this methodology is performed by simultaneous irradiation of Mo and U standards with well known masses. The activity of the ^{99}Mo is measured by the characteristic gamma ray transitions; the intensity of these gammas and half-life of this radioisotope are presented in Table 1.

Table 1: Gamma lines, intensity and half life used in determination of uranium fission interference factor for Mo

Radioisotope	Eγ (keV) [8]	Intensity (%) [8]	Half life (h) [8]
^{99}Mo	181.06	6.08	65.94
^{99}Mo	739.5	12.13	65.94
^{99}Mo	140.51	90.70	65.94

The determination of interference factor by the 140.51 keV of ^{99}Mo requires attention, because this gamma ray is emitted in the ^{99m}Tc decay, therefore the radioactive equilibrium between the ^{99m}Tc and ^{99}Mo must be reached. In the present work the decay time before the samples were analyzed was about 6 days, to wait a necessary decay time to handle the irradiated samples.

The specific activity of the ^{99}Mo from ^{98}Mo neutron capture and the specific activity from the uranium fission can be calculated using the equations 3 and 4 [9], respectively:

$$A^{Mo} = \frac{a_{Mo} N_0}{M_{Mo}} (\phi_{th}\sigma_{th}^{Mo} + \phi_{ep}\sigma_{ep}^{Mo}) \cdot (1 - e^{\lambda_{Mo} t_{irrad}}) \tag{3}$$

$$A_U^{Mo} = \frac{a_U N_0 f_{Mo}}{M_U} (\phi_{th}\sigma_{th}^{U} + \phi_{ep}\sigma_{ep}^{U}) \cdot (1 - e^{\lambda_{Mo} t_{irrad}}) \tag{4}$$

Where a_{Mo} and a_U are isotopic abundances of ^{98}Mo and ^{235}U; M_{Mo} and M_U are the Mo and U atomic masses; N_0 is the Number of Avogadro; f_{Mo} is the cumulative fission yield for ^{99}Mo; ϕ_{th} and ϕ_{ep} are thermal and epithermal neutron fluxes; σ_{th}^{Mo} and σ_{ep}^{Mo} are thermal and epithermal neutron capture cross sections of ^{98}Mo; σ_{th}^{U} and σ_{ep}^{U} are the ^{235}U fission cross sections for thermal and epithermal neutron fluxes; λ^{Mo} and t_{irrad} are the ^{99}Mo decay constant and the irradiation time.

Using equations 3 and 4 the interference factor for Mo can be determinedas:

$$F_{Th}^{Mo} = \frac{M_{Mo} a_U f_{Mo} \left[\sigma_{th}^{U} + (\phi_{ep} / \phi_{th}) \cdot \sigma_{ep}^{U} \right]}{M_U a_{Mo} \left[\sigma_{th}^{Mo} + (\phi_{ep} / \phi_{th}) \cdot \sigma_{ep}^{Mo} \right]} \tag{5}$$

This methodology of calculation gives the interference factor called *theoretical interference factor*. To determine the Mo interference factor using equation 5 the epithermal to thermal neutron fluxes ratio must be measured, and the nuclear parameters reported in literature presented in Table 2 must be used.

Table 2: Nuclear parameters used to determinate the theoretical interference factor

Nuclear reaction	Isotopic abundance [8]	Atomic mass (u) [10]	$\sigma_{th}{}^{a}$ (b) [11]	$\sigma_{ep}{}^{b}$ (b) [11]	Cumulative fission yield [12]
$^{98}Mo(n,\gamma)^{99}Mo$	0.2413	95.94	0.137 ± 0.02	6.9 ± 0.3	0.06132
$^{235}U(n,f)$	0.0072	238.029	582	275	-

a. thermal neutron cross section; *b*. epithermal neutron cross section

3. MATERIALS AND METHODS

3.1. Preparation, Irradiation and Measurement of Activities of Mo and U Synthetic Standards

The synthetic standards of Mo and U were prepared pipetting 50 μL of diluted certified standard solutions onto sheets of Whatman N_0. 40 filter paper. These diluted solutions were prepared using stock solutions of Mo and U provided by Spex Certiprep, USA. These sheets were dried into a desiccator for about 24 h, and they were placed into a polyethylene bags previously cleaned using diluted nittic solution and purified water. The masses of U and Mo used were (10.030 ± 0.030) μg and (6.018 ± 0.018) μg, respectively.

These standards were irradiated together inside the same irradiation device in IEA-R1 nuclear research reactor in the position 14b shelf 3 for 8 h. The induced activities of the synthetic standards were measured using a hyperpure Ge detector model GC1930 coupled to a Digital Spectrum Processor DSA 1000, both from Canberra Industries. The nominal resolution of the system was 0.90 keV for the 122 keV gamma ray peak of ^{57}Co and 1.80 keV of 1332 keV gamma ray peak of ^{60}Co. The time of counting was 5400 s for Mo and about 9000 s for U. These measurements were carried out in the same counting geometry, and the gamma rays spectra were collected and analyzed using the Canberra Genie 2000 software, version 3.1 [13].

The activities of these standards were measured in three different decay times: after 6, 13 and 21 days.

3.2. Determination of Thermal and Epithermal Neutron Fluxes

The determinations of epithermal and thermal neutron fluxes were necessary to obtain the *theoretical interference factor*.The cadmium ratio technique was used in order to determine the epithermal to thermal neutron fluxes ratio [9].

The certified reference material IRMM 530-R of Au-Al alloy with 0.1 % of Au provided by Institute of Reference Materials and Measurements was used as neutron flux monitor. This alloy was cleaned with isopropyl alcohol and then cut and weighted. The used mass was of about 3.5 mg.

In order to obtain the epithermal and thermal neutron fluxes one monitor was irradiated inside a cadmium capsule and the other without the cadmium capsule, both inside of the same irradiation device, for an irradiation time of 4 h. The flux monitors were irradiated in the same position used forthe synthetic standards irradiations.

The activities were measured by the 411 keV gamma ray of ^{198}Au (half life of 2.69 d) [8] in a decay time of about 7 d using the acquisition system described in section 3.1.

4. RESULTS AND DISCUSSION

Six irradiations were carried out to determine the mean value for epithermal and thermal neutron fluxes. The mean value obtained to epithermal and thermal neutron fluxes were $\phi_{ep} = (1.10 \pm 0.04) \cdot 10^{11} n \cdot cm^{-2} \cdot s^{-1}$ and $\phi_{th} = (8.36 \pm 0.06) \cdot 10^{12} n \cdot cm^{-2} \cdot s^{-1}$.The epithermal to thermal neutron fluxes ratio obtained using these values was $\phi_{epi} / \phi_{th} = 0.013 \pm 0.001$.This value was used in equation 4 to determine the *theoretical interference factor*. The obtained value (in μg Mo/μg U) was $F_{Th}^{Mo} = 2.03 \pm 0.08$.

The experimental interference factor was determined by performing 17 irradiations of synthetic standards. The recommended gamma ray for ^{99}Mo measurement by IAEA [8] is the 739.58 keV. However other gamma transitions presented in Table 1 were also used in this study. The *experimental interference factor* values obtained with these gamma rays for ^{99}Mo are presented in Table 3.

Table 3: Experimental interference factor obtained for ^{99}Mo

Eγ (keV)	$F_{Ex}^{Mo} \pm SD^{a}$	RSD[b] (%)
181.06	2.00 ± 0.17	8.5
739.5	2.04 ± 0.04	1.9
140.51	2.00 ± 0.08	4.0

a. Experimental interference factor for ^{99}Mo with standard deviation; b. Relative standard deviation.

The *experimental interference factor* determined using the 181.06 keV gamma ray energy is close to the values obtained from the 739.5 keV and 140.51 keV transitions. However, the relative standard deviation points to lower precision as can be seen in Table 3. The interference factor that presented the lowest relative standard deviation was that obtained using the 739.5 keV gamma rays. The theoretical and experimental values obtained presented a good agreement. This result indicates that the determined epithermal to thermal neutron fluxes ratio and the parameters used allowed to obtain reliable result of theoretical interference factor.

Due to the strong dependence of the uranium fission product interference with the epithermal to thermal neutron fluxes ratio, it is expected that factors obtained by different authors present some variability. In Table 4 are presented theoretical and experimental values obtained in this study and the ones reported in the literature, as well as the neutron fluxes ratios.

Table 4: Neutron flux ratios, theoretical and experimental interference factors for ^{99}Mo and literature reported values

Reference	$\phi_{epi}/\phi_{th} \pm SD^a$	$F_{Th}^{Mo^b} \pm SD$	$F_{Ex}^{Mo^c} \pm SD$
Glascock, et al. [5]	0.0201 ± 0.0018	1.67 ± 0.10	1.40 ± 0.05
Landsberg [6]	0.033 ± 0.006	1.26 ± 0.15	1.70 ± 0.10
Park, et al. [7]	0.0239 ± 0.0007	1.52 ± 0.06	1.36 ± 0.19
Martinho, et al. [1]	0.00023 ±0.00007	3.38 ± 0.16	2.70 ± 0.10
	0.0120 ±0.00060	2.10 ± 0.09	1.90 ± 0.10
	0.0208 ±0.00170	1.64 ± 0.09	1.31 ± 0.05
	0.0301 ±0.00230	1.33 ± 0.08	1.05 ± 0.04
This study	0.0130 ±0.00052	2.03 ± 0.08	2.04 ± 0.04

a. standard deviation; b. theoretical interference factor for ^{99}Mo; c. experimental interference factor for ^{99}Mo.

As seen in Table 4, the theoretical and experimental interference factors for ^{99}Mo obtained by different authors present variations depending on the neutron flux ratios. Besides, some literature values of interference factors show differences between the results obtained theoretically and experimentally.

As previously mentioned, high values of interference factors due to fission of uranium can lead to substantial systematic errors. The relative error in a determination of Mo can be evaluated using equation 6.

$$Relative\ Error = \frac{F^{Mo} \times [U]}{[Mo]_{true}} \times 100 \quad (6)$$

Where [U] is the U concentration in the sample and $[Mo]_{true}$ is the real concentration of Mo in the sample.

Using equation 6, the dependence of relative error with [U]/[Mo]concentration ratio can be plotted, as shown in Fig. 1.

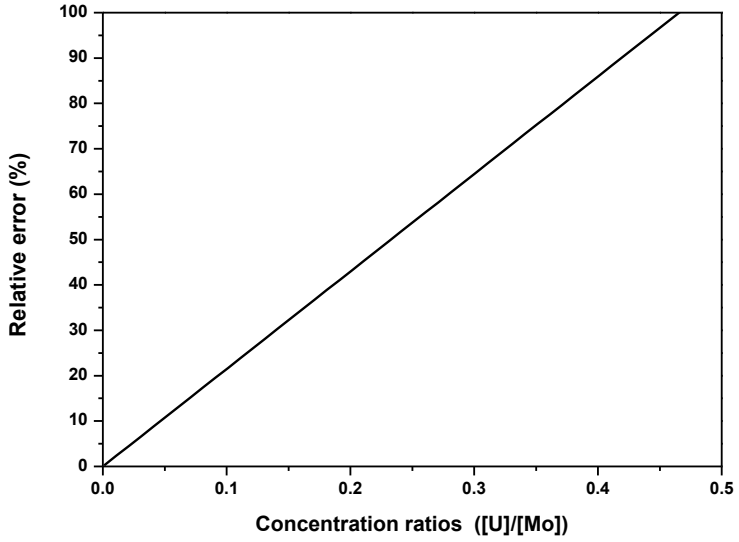

Figure 1: Relative error for different ratios between U and Mo concentrations.

Fig. 1 shows that if the interference due to uranium fission is not considered in Mo determination by INAA, the results obtained for example for a sample with 0.1 ppm of U per 1 ppm of Mo can provide results with a relative error of 20 % due to U fission product interference.

5. CONCLUSIONS

The good agreement between theoretical and experimental values of uranium fission interference factor for the ^{99}Mo indicates that both theoretical and experimental ways can be used to obtain it.

From the result obtained it can conclude that the contribution of interference of ^{99}Mo fission product is very serious. For example, the magnitude of the relative error due to uranium fission interference in the determination of concentration of Mo by INAA can cause an error of 20% in the case when the concentration of Mo is 10 times larger than of the U.

The next step of this study will be the application of the uranium fission interference factor for ^{99}Mo obtained in this work in the analysis of certified reference material in order to evaluate the accuracy of the results.

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