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Samarium determination by neutron activation analysis in uranium-rich samples

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Abstract In this work, an alternative method to determine the U interference factor for ^{153}Sm as a function of the decay time was studied aiming to take into account the time dependence arising from the spectral interference of ^{239}Pu X-rays. An experimental interference factor and a theoretical equation dependent on the epithermal and thermal neutron fluxes and on the decay time were also proposed. These interference factors obtained from both, experimentally and using the theoretical equation were applied on the correction of the Sm concentration in the BCR-667 certified reference material with good results, showing the reliability of these correction factors.

Keywords Neutron activation analysis · Samarium · Uranium fission interference factor · Correction factor

Introduction

Instrumental neutron activation analysis (INAA) is an analytical technique used to determine the mass fraction of several elements in different types of matrices. However, in uranium-rich samples, the determination of some elements can be affected when the radioisotopes produced by uranium fission interfere with the elements used in the determination of the element of interest. Since the magnitude of this interference depends on the epithermal-to-thermal neutron flux ratio, the U fission interference factor must be determined for the elements of interest in a particular irradiation facility and then use these interference factors to correct the concentrations of the elements.

Sm is one of the elements that can be determined by INAA, but it suffers interference when the sample contains U. In this case of the Sm, the determination of U interference factor is more complex, as not only does the fission of ^{235}U produce ^{153}Sm, but also x-rays from ^{239}Pu, originated in the neutron capture of ^{238}U, having the same energy as the 103 keV gamma transition used in the determination of Sm. Moreover, this interference is time-dependent, as the half-lives involved in the production and decay of ^{239}Pu are significantly different from the half-life of ^{153}Sm. The determination of U fission interference factor for ^{153}Sm has been widely studied [1–11], but no effective; practically applicable result has been reached, and the problem of Sm determination in U-rich samples was left to other techniques usually requiring digestion and chemical separation [10]. In this study, a U interference factor was determined as a function of the decay time and that can be applied to determine Sm concentration by INAA in uranium-rich samples.

Uranium fission interference factor

The uranium fission interference factor is defined as the ratio between the specific activity of the radioisotope formed by the fission of U and the specific activity of the radioisotope formed by the (n,γ) reaction. This factor (F_X) can be determined experimentally by irradiating both standard of U and of the element in question, and then using Eq. (1) [12].

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$$F_X = \frac{A_U^X / m_U}{A_X / m_X} \quad (1)$$

where m_X and m_U are the mass of the element of interest and of U, respectively; A_U^X and A_X are the induced activities by U fission and (n,γ) reaction of element to be determined..

Furthermore, the induced activities A_U^X and A_X can be calculated using experimental measurements of the thermal and epithermal neutron fluxes (φ_{th} and φ_{ep}, respectively) as follows:

$$A_U^X = \frac{m_U \times a_{^{235}U} \times N_A \times f_X \times I^\gamma \times \varepsilon}{M_U} \times \left(\sigma_{th}^{U^{235}(n,f)} \times \varphi_{th} + \sigma_{ep}^{U^{235}(n,f)} \times \varphi_{ep}\right) \times \left(1 - e^{-\lambda_X \times t_i}\right) \quad (2)$$

$$A_X = \frac{m_X \times a_X \times N_A \times I^\gamma \times \varepsilon}{M_X} \times \left(\sigma_{th}^{X(n,\gamma)} \times \varphi_{th} + \sigma_{ep}^{X(n,\gamma)} \times \varphi_{ep}\right) \times \left(1 - e^{-\lambda_X \times t_i}\right) \quad (3)$$

where the indices X and U refer to the element of interest and uranium, respectively; M is the atomic weight; a is the isotopic abundance; N_A is Avogadro's constant; f is the cumulative fission yield; I^γ is the gamma transition intensity; ε is the detection efficiency; $\sigma_{th}^{U^{235}(n,f)}$ and are $\sigma_{ep}^{U^{235}(n,f)}$ the thermal and epithermal fission cross sections, respectively; λ is the decay constant of the radioisotope; $\sigma_{th}^{X(n,\gamma)}$ and $\sigma_{ep}^{X(n,\gamma)}$ are capture cross sections for thermal and epithermal neutrons, respectively and t_i is the irradiation time.

Using Eq. (2) and (3), the interference factor can be determined theoretically using the following equation:

$$F = \frac{M_X \times a_{^{235}U} \times f_X \times \left[\sigma_{th}^{U^{235}(n,f)} + \left(\varphi_{ep}/\varphi_{th}\right) \times \sigma_{ep}^{U^{235}(n,f)}\right]}{M_U \times a_X \times \left[\sigma_{th}^{X(n,\gamma)} + \left(\varphi_{ep}/\varphi_{th}\right) \times \sigma_{ep}^{X(n,\gamma)}\right]} \quad (4)$$

U interference factor for ^{153}Sm

The determination of the uranium interference factor for ^{153}Sm ($t_{1/2}$ = 46.75 h) is a special case, because Sm determination by INAA is usually carried out using 103 keV transition from the decay of the ^{153}Sm radioisotope. In this case, when the sample contains uranium, in addition to the small interference due to uranium fission, there is a strong spectral interference arising from the 103 keV X-ray emitted in the internal conversion of the $K_{\alpha 1}$ shell of ^{239}Pu, which is produced in uranium irradiation as shown in Fig. 1.

Due to this additional interference on the 103 keV transition, in this particular case the Eq. (1) must be rewritten as:

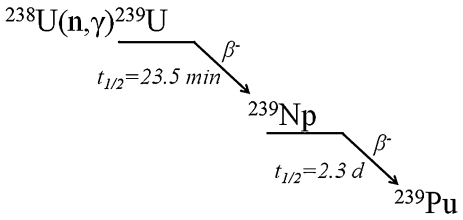

Fig. 1 ^{239}Pu production in the neutron irradiation of uranium

$$F_{^{153}Sm} = \frac{A_U^{^{153}Sm} + A_{^{239}Np}^{X-ray}}{A_{^{153}Sm}} \times \frac{m_{Sm}}{m_U} = \frac{A_{103\,keV}^{total}}{A_{^{153}Sm}} \times \frac{m_{Sm}}{m_U} \quad (5)$$

where the terms $A_U^{^{153}Sm}$ and $A_{^{239}Np}^{X-ray}$ are the activities due to ^{153}Sm from U fission and ^{239}Pu X-rays from U neutron capture.

The half-life of ^{239}Np is larger than that of ^{153}Sm, therefore the interference factor for ^{153}Sm will increase with the decay time. Considering the (n,γ) reaction and the β^- decay of ^{239}Np during the irradiation, and noting that the activity of the ^{239}Pu X-rays decreases with the half-life of ^{239}Np, an effective U interference factor for ^{153}Sm can be calculated theoretically as a function of the decay time by means of the following equation:

$$F_{^{153}Sm}(t_d) = \overbrace{\frac{M_{Sm} \times a_{^{235}U} \times f_{^{153}Sm}}{M_U \times a_{^{152}Sm}}}^{A = (2.52 \pm 0.12) \times 10^{-5}} \times \frac{k_{^{235}U}^f}{k_{^{152}Sm}^{(n,\gamma)}} + \overbrace{\frac{I^{X-ray} \times \lambda_{^{239}Np} \times M_{Sm}}{I^\gamma \times a_{^{152}Sm} \times N_0}}^{B = (2.33 \pm 0.07) \times 10^{-27}} \times \frac{N_0^{^{239}Np} \times e^{-t_d \cdot \left(\lambda_{^{239}Np} - \lambda_{^{153}Sm}\right)}}{k_{^{152}Sm}^{(n,\gamma)} \times \left(1 - e^{-\lambda_{^{153}Sm} \times t_i}\right)} \quad (6)$$

where for the sake of simplicity, some terms linked to ^{235}U fission and ^{152}Sm neutron capture were grouped as:

$$k_{^{235}U}^f = \sigma_{th}^{U^{235}(n,f)} \times \varphi_{th} + \sigma_{ep}^{U^{235}(n,f)} \times \varphi_{ep};$$

$$k_{^{152}Sm}^{(n,f)} = \sigma_{th}^{^{152}Sm(n,f)} \times \varphi_{th} + \sigma_{ep}^{^{152}Sm(n,f)} \times \varphi_{ep};$$

and t_d is the decay time after irradiation, I^{X-ray} is the absolute intensity of the x-ray emitted by ^{239}Pu and $N_0^{^{239}Np}$ is the number of atoms of ^{239}Np formed after irradiation. The parameter $N_0^{^{239}Np}$ is a function of the irradiation time and can be determined using Eq. (7):

$$N_0^{^{239}Np}(t_i) = \overbrace{\frac{m_U \times a_{^{238}U} \times N_A}{M_U \times \lambda_{^{239}Np} \times \left(\lambda_{^{239}Np} - \lambda_{^{239}U}\right)}}^{C = (-1.513 \pm 0.002) \times 10^{25}} \times k_{^{238}U}^{(n,\gamma)} \times \left[\lambda_{^{239}Np} \times \left(1 - e^{-\lambda_{^{239}U} \times t_i}\right) - \lambda_{^{239}U} \times \left(1 - e^{-\lambda_{^{239}Np} \times t_i}\right)\right] \quad (7)$$

where $k_{^{238}U}^{(n,\gamma)} = \sigma_{th}^{^{238}U(n,\gamma)} \times \varphi_{th} + \sigma_{ep}^{^{238}U(n,\gamma)} \times \varphi_{ep}$.

Therefore the *effective* U *interference factor* for ^{153}Sm can be calculated using nuclear parameters and the values of epithermal and thermal neutron fluxes under the same irradiation conditions where the experimental interference factors were determined, as shown in Eqs. (6) and (7). The nuclear parameters used to determine this theoretical U fission interference factor are presented in Table 1.

Calculation of Sm concentration using U interference factor

Considering the interference due to ^{235}U fission and the x-rays from ^{239}Pu, the corrected concentration of Sm in uranium-rich samples is obtained by the following equation:

$$[Sm]_{true} = [Sm]_{app} - F_{^{153}Sm} \times [U] \quad (8)$$

where $[Sm]_{true}$ and $[Sm]_{app}$ are the true concentration and apparent concentration, respectively; $F_{^{153}Sm}$ is the *effective* U interference factor for ^{153}Sm, and [U] is the U concentration in the same sample.

Experimental

Preparation of synthetic standards

For the preparation of the 18 synthetic standards of Sm and U, standard element solutions provided by Spex Certiprep USA were diluted in purified water. The standard of U used in this study contains natural isotopic abundance. 50 μL of these diluted solutions were pipetted onto Whatman No. 40 filter paper, which were subsequently dried at room temperature for 24 h inside a desiccator and then heat-sealed into clean polyethylene bags. The total mass of Sm and U pipetted onto these sheets were (in ng): 10,010 (20) and 10,030 (203), respectively.

Neutron flux determination

The cadmium ratio technique was used to determine the epithermal and thermal neutron fluxes. A gold–aluminum alloy of certified reference material IRMM-530R, with 0.1 % of gold was used as flux monitors. These flux monitors, with approximately 3.5 mg each, were cleaned using isopropyl alcohol, and then irradiated for 4 h at the same position as the synthetic standards. For neutron flux determination 8 irradiations were carried out.

Reference material preparation

In the present study, the concentration of Sm in the BCR-677 Estuarine Sediment certified reference material was determined. In order to present result on dry weight base, an aliquot of this material was dried at 105 °C according to the certificate of this material. For the analysis of Sm, four aliquots of this reference material, weighing about 120 mg each, were irradiated in the reactor.

Irradiations

All irradiations of synthetic standards, flux monitors and certified reference material were carried out in position 14b, shelf 3, at the IEA-R1 nuclear research reactor of IPEN-CNEN/SP. The synthetic standards, flux monitors and reference material were irradiated inside the same irradiation device for 8 h. About 4 days after the end of the irradiation, they were mounted in planchets for gamma ray measurements.

Activity measurements

The activity measurements were carried out using a hyperpure Ge detector Model GC1930 coupled to a Digital Spectrum Processor DSA1000, both from Canberra. The resolution (FWHM) of the system is 0.90 keV for the 122 keV gamma-ray peak of ^{57}Co and 1.8 keV for the 1332 keV gamma ray of ^{60}Co. The measurements were carried out in different decay times, with counting times ranging from 3600 to 36,000 s, depending on the half-lives and activities of the radioisotopes considered. Gamma spectra were collected and processed using Canberra Genie 2000 Version 3.1 software.

Table 1 Nuclear parameters used in the calculation of uranium interference factor

Nuclear reactions	Isotopic abundance [13]	Atomic weight	$\sigma_{Th\ flux}$ (b) [14]	$\sigma_{Epth\ flux}$ (b) [14]	Cumulative fission yield [16]	Half-life (d) [15]
$^{152}Sm(n,\gamma)^{153}Sm$	0.267	150.36	206 (6)	2970 (100)	0.001477	1.92855(5)
$^{239}Np(n,\gamma)^{240}Np$	–	–	68 (10)	455	–	2.356 (3)
$^{238}U(n,\gamma)^{239}U$	0.992745	238.029	2.680 (19)	277 (3)	–	0.01629(3)
$^{235}U(n,f)$	0.0072	238.029	582	275	–	–

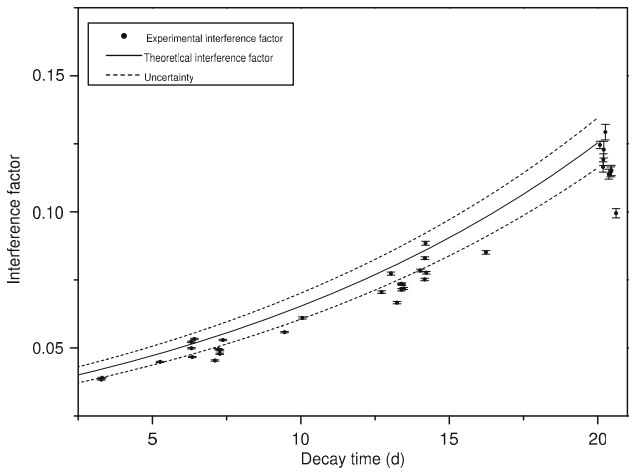

Fig. 2 Theoretical and experimental interference factor as a function of the decay time

Table 2 Obtained concentration of Sm in BCR-667 Estuarine Sediment certified reference material in mg kg^{-1}

Reference Material	$[Sm]_{app}$	$[Sm]_{true}$	Certified concentration	z-score
BCR-667 estuarine sediment	5.06 ± 0.05	4.94 ± 0.66	4.66 ± 0.19	1.01

Results and discussion

The obtained values for the *experimental interference factor* (using the activity measurements) ranged from $(3.84 \pm 0.02) \times 10^{-2}$, for 3.3 days of decay time, to $(1.23 \pm 0.03) \times 10^{-1}$, for 20 days of decay time; therefore, there was an increase of the interference factor with the decay time, as expected. Also, a theoretical value for this interference factor as a function of time was determined using the Eq. (6) and the measured values of the thermal and epithermal neutron fluxes were $(5.37 \pm 0.39) \times 10^{12}$ and $(6.93 \pm 0.58) \times 10^{10}$ $cm^{-2}s^{-1}$, respectively.

Figure 2 shows the results of the *experimental* (points) and *theoretical* (curve) interference factors obtained in this study. These results indicate agreement between the obtained results using both methods; the considerable uncertainty of the theoretical interference factor (dotted curve) originates mainly from the large relative standard deviation of the thermal and epithermal neutron fluxes, respectively 7.30 and 8.37 %. The results of experimental and theoretical interference factors can be considered compatible considering the uncertainties values of the results.

It is important to notice that the theoretical interference factor obtained by Eq. (4), where the interference from the Pu X-rays is not taken into account, was $(6.03 \pm 0.66) \times 10^{-5}$, while the values obtained for the *experimental interference factor* after 3 days of decay time was $(3.84 \pm 0.02) \times 10^{-2}$. In other words, the experimental interference factor is approximately 500 times larger than the theoretical interference factor, showing that most of the interference is due to the X-rays from ^{239}Pu.

The *experimental interference factor* obtained at the same decay time (6.4 days) of the CRM was used in the Sm concentration determination in this certified reference material. Both, experimental and theoretical values of interference factor, leads to similar results. The true, apparent and certified concentrations of Sm are shown in Table 2.

It can be noted that the use of the effective interference factor improved the obtained results, showing the usefulness of this correction. It should be stressed that if the experimental factor is used, it must be determined in the same decay time of the analyses; on the other hand, if the theoretical factor is used, one should make sure that the epithermal and thermal neutron flux used are correct.

Conclusions

The interference in the 103 keV peak used in the ^{153}Sm measurements increases with the decay time due to the X-rays from ^{239}Pu, which is produced by neutron capture in the ^{238}U present in the sample. Moreover, this interference from X-ray from ^{239}Np is larger than the interference arising from the production of ^{153}Sm via uranium fission. An *effective* U *correction factor* was experimentally and theoretically determined. Both approaches led to similar values, showing that either approach can be safely used.

In conclusion, the use of experimental and theoretical factors in the determination of Sm in BCR 677 estuarine sediment certified reference material indicated that these factors are suitable for practical applications.

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