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Determination of ^{235}U abundance in uranium by neutron activation on the basis of the molybdenum fission interference

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The purpose of the present paper is to suggest a method for determining the ^{235}U abundance in uranium samples (compounds, metallic alloys or other uranium materials, where this element may be natural or not) through a particular application of neutron activation analysis, based on the fission interference by molybdenum. The method lies on an a priori calibration with natural uranium, thus it does not require ^{235}U certified standards.

Introduction

Experience reveals that one finds on the market compounds, metallic alloys and other uranium materials where this element is depleted of ^{235}U. This happens frequently and is due to the production of enriched uranium. For certain experiments involving the utilization of neutron activation analysis (NAA), one needs to use uranium of a high degree of nuclear purity, but with the natural abundance in ^{235}U or with a known isotopic composition. At present market conditions, there may therefore be an interest in knowing whether the uranium which is present in a given material is natural or depleted. On the other hand, an expert in NAA may be asked to determine the ^{235}U abundance in a given uranium sample, either a natural, depleted or slightly enriched one.

The ^{235}U abundance can be determined using several analytical techniques, such as isotope dilution mass spectrometry and alpha-radiation spectrometry, for example. NAA can also be used on the basis of an ^{235}U certified standard. The purpose of the present paper is to suggest a method for determining the ^{235}U abundance through a particular application of the NAA technique, on the basis of the fission interference concerning molybdenum, which does not require ^{235}U certified standards.

Basis of the method

Fission interference in NAA

It is known that, when using NAA for multielemental analysis of samples containing uranium, the presence of uranium interferes with the determination of the concentration of a certain number of elements (Ba, Ce, La, Mo, Nd, Ru, Zr, etc.).[1] This is generally due to a given fission product [reaction $^{235}U(n,f)^{A+1}X$] and the radionuclide which is produced by radiative capture of neutrons in a given isotope of the natural element to be analysed [reaction $^{A}X(n,\gamma)^{A+1}X$, where ^{A+1}X is the radionuclide used for determining the concentration of the element X] being identical. This makes it necessary to carry out a fission interference correction concerning the elements referred above, otherwise one may incur in coarse errors when determining their concentration.

The expression for the fission interference correction is as follows:

$$[X]_{true} = [X]_{app} - F_X[U]$$

where $[X]_{true}$ and $[X]_{app}$ is the actual and the apparent (observed) concentration, respectively, of the element X in the sample, [U] the uranium concentration in the same sample, and F_X the correction factor for the fission interference concerning element X (F_X is expressed, for example, as ppm of X per ppm of uranium).

The general definition of the fission interference factor is:

$$F_X = \frac{A^*_{sp}\left(^{A+1}X\right)}{A_{sp}\left(^{A+1}X\right)} \quad (1)$$

where $A_{sp}(^{A+1}X)$ is the specific activity of ^{A+1}X induced by radiative capture of neutrons in the element X, and $A^*_{sp}(^{A+1}X)$ is the specific activity of the same radionuclide induced by nuclear fission reactions in uranium.

Fission interference factor for molybdenum

The ^{99}Mo is the indicator nuclide of interest for the present method. In Figure 1, the block-diagrams corresponding to the production of ^{99}Mo by nuclear fission of ^{235}U in the uranium sample and by radiative capture of neutrons in a natural molybdenum sample is shown, and the nuclear data relevant for the calculation are given.[2–6] The schemes on Fig. 1 present a simplified version of those which were used in a previous work,[7] but they are found to be sufficient for modeling the calculation, because the effect of the double capture of neutrons is negligible, and the half-lives of the fission products of the decay chain corresponding to the mass number A = 99 is much smaller than that of the half-life of ^{99}Mo (66 hours).

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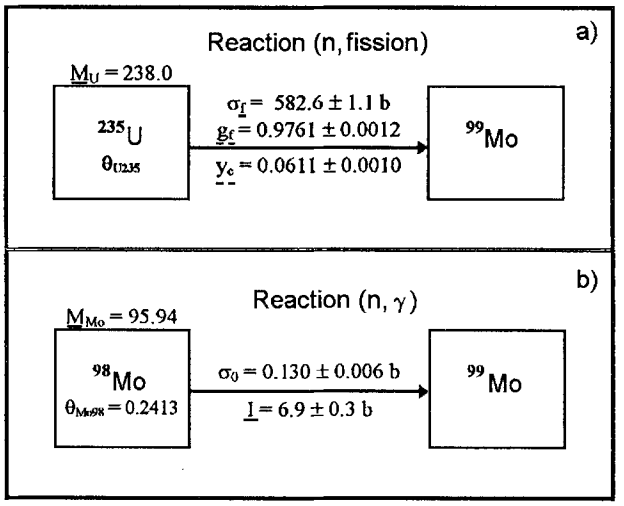

Fig. 1. Block-diagrams corresponding to: (a) the production of ^{99}Mo by (n, fission) reaction in uranium; (b) the formation of ^{99}Mo by (n,γ) reaction in molybdenum

Using the definition of the fission interference factor [Eq. (1)] and the concept of effective neutron cross section from the WESTCOTT formalism,[8] one can show that the fission interference correction factor concerning molybdenum, F_{Mo}, is given, with a very good approximation, by the expression:[9]

$$F_{Mo} = \frac{M_{Mo}\theta_{U235}y_c}{M_U\theta_{Mo98}} \frac{g_f\sigma_f}{\sigma_0 + \frac{2}{\sqrt{\pi}} I \frac{\Phi_{epi}}{\Phi_0}} \qquad (2)$$

where:

M_{Mo} – atomic mass of natural molybdenum,

M_U – atomic mass of uranium ($M_{Unat} = 238.03$; $M_{U238} = 238.05$),

θ_{Mo98} – ^{98}Mo abundance in the natural molybdenum,

θ_{U235} – ^{235}U abundance in uranium ($\theta_{U235} = 0.720$ atom % in U_{nat}),

y_c – cumulative fission yield of ^{99}Mo for the thermal neutron fission of ^{235}U,

σ_0 – thermal neutron cross section for the $^{98}Mo(n,\gamma)^{99}Mo$ reaction,

I – neutron resonance integral for the $^{98}Mo(n,\gamma)^{99}Mo$ reaction,

σ_f – thermal neutron cross section for the ^{235}U(n,fission) reaction,

g_f – Westcott factor concerning the thermal neutron fission cross section of ^{235}U.

As can be seen in Fig. 2, there is an excellent agreement between the experimental values of F_{Mo} for natural uranium[10–15] (see Table 1) and the calculated values using Eq. (2) as a function of the epithermal to thermal neutron flux ratio, Φ_{epi}/Φ_0. Thus, ^{99}Mo is suggested as the indicator nuclide in the proposed method for the following reasons: (a) the calculation of F_{Mo} can be considered as being well validated through the experimental data found in the literature for natural uranium and for the usual irradiation conditions ($\Phi_{epi}/\Phi_0 < 0.05$), (b) the modeling of the calculation does not depend on any restrictive hypothesis concerning the ^{235}U abundance values, and thus the model should be valid also for values of $\theta_{U235} \neq 0{,}72\%$, (c) it is possible to determine F_{Mo} with a relatively small uncertainty, and (d) the value of F_{Mo} depends strongly on the Φ_{epi}/Φ_0 ratio, a fact which can be used for ensuring a higher quality for the θ_{U235} results to be obtained, using independent and fairly distinct experiments.

Determination of the ^{235}U abundance

Equation (2) may be written to give the ^{235}U abundance explicitly:

$$\theta_{U235} = \frac{M_U\theta_{Mo98}}{M_{Mo}y_c} \times \frac{\sigma_0 + \frac{2}{\sqrt{\pi}} I \frac{\Phi_{epi}}{\Phi_0}}{g_f\sigma_f} \times F_{Mo} \qquad (3)$$

One should note that, in general, θ_{U235} is a function of F_{Mo} and of Φ_{epi}/Φ_0, because the other parameters are nuclear constants. The abundance of θ_{U235} depends exclusively on F_{Mo} only in the case where identical irradiation conditions are used (Φ_{epi}/Φ_0 = constant).

In order to apply the method, one can use two alternative ways for determining θ_{U235} by means of Eq. (3): (1) one way is just to carry out one single experimental determination of F_{Mo} with an uranium sample to be analysed, at an irradiation facility where the Φ_{epi}/Φ_0 ratio may be well known; (2) another, more safe, way of using the method consists in repeating it,

preferably by using different irradiation conditions. In this case, one should carry out two (or more) determinations of F_{Mo} with different samples of the uranium to be analysed, using irradiation facilities for which the Φ_{epi}/Φ_0 ratio may have well known and as distinct values as possible.

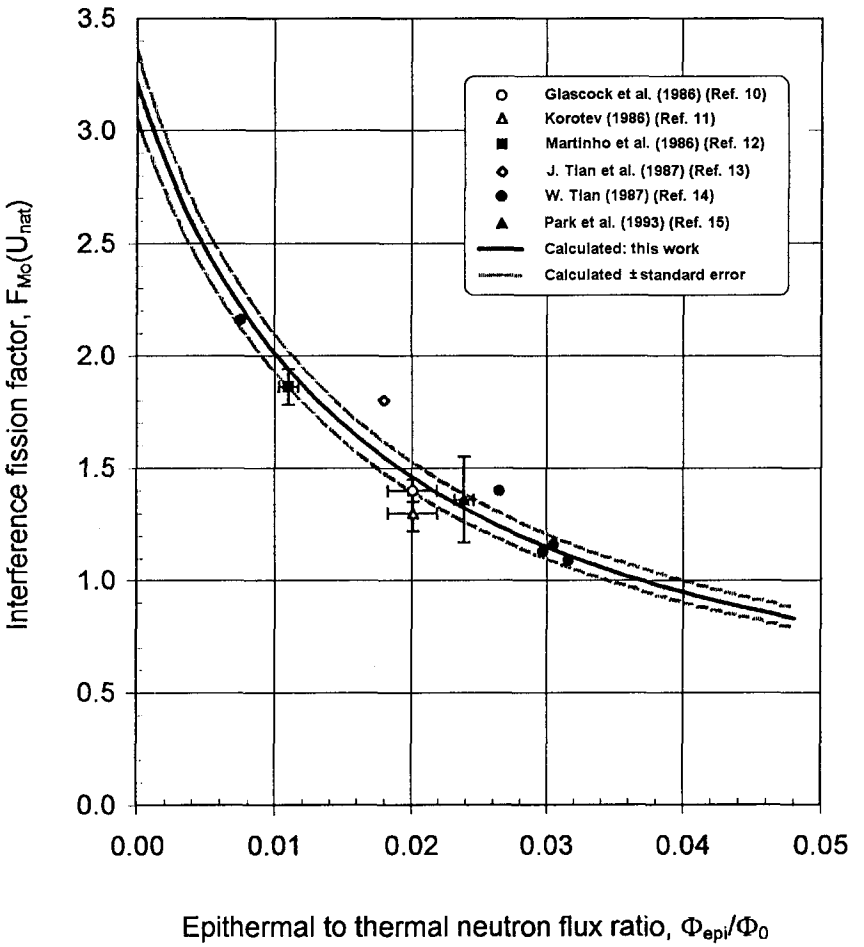

Fig. 2. Comparison between experimental and calculated values of fission interference factor for molybdenum, $F_{Mo}(U_{nat})$, as a function of Φ_{epi}/Φ_0

Table 1. Experimental fission interference factor for molybdenum, $F_{Mo}(U_{nat})$, as a function of the epithermal to thermal neutron flux ratio Φ_{epi}/Φ_0

Reference	Thermal neutron flux (Φ_0) $cm^{-2}s^{-1}$	Ratio of neutron fluxes (Φ_{epi}/Φ_0)	Fission interference factor (U_{nat}) (F_{Mo})	Observation
GLASCOCK et al. (1986)[10]	$5.3 \cdot 10^{13}$	0.0201±0.0018	1.40±0.05	
KOROTEV (1986)[11]	$5.3 \cdot 10^{13}$	0.0201±0.0018	1.28±0.08	Same position and same reactor as GLASCOCK et al. (1986)
MARTINHO et al. (1986)[12]	$1.4 \cdot 10^{11}$ (1)	0.011±0.001(2)	1.86±0.08	(1)Revised value (LOPES et al., 1986)[16] (2)Estimated value.
J. TIAN et al. (1987)[13]	$4 \cdot 10^{13}$	0.018(3)	1.8	(3)Value derived from $\Phi_{epi} = 7.3 \cdot 10^{11}$ n $\cdot cm^{-2} \cdot s^{-1}$ given by CARNI (1986)[17]
W. TIAN (1987)[14]	$4–6 \cdot 10^{13}$	0.0075	2.16	$\Phi_{epi}/\Phi_0 = 1/f$, where f is the parameter of the
	$4–6 \cdot 10^{13}$	0.0265	1.40	k_0–method which has been measured by the author
	$3.5 \cdot 10^{13}$	0.0297	1.13	
	$4–6 \cdot 10^{13}$	0.0305	1.16	
	$3.5 \cdot 10^{13}$	0.0316	1.09	
PARK et al. (1993)[15]	$4 \cdot 10^{12}$	0.0239±0.0007	1.36±0.19	

Application of the method

Determination of the fission interference factor for molybdenum

The experimental determination of the fission interference factor F_{Mo} requires the simultaneous irradiation of a sample of natural molybdenum and of a sample of the uranium to be analysed, at an irradiation facility where the Φ_{epi}/Φ_0 ratio is well known. After the irradiation, and after an appropriate waiting time, one determines the activity of ^{99}Mo of both samples in a gamma-radiation spectrometer with a high energy resolution detector. This requirement is mainly due to the existence of numerous fission products in the uranium sample.

For determining the ^{99}Mo activity, one should recall its decay scheme:

$$^{99}Mo \xrightarrow{\beta^-;T_{1/2}=65.9\,h;E_\gamma=739.5\,keV} {}^{99m}Tc \xrightarrow{\gamma;T_{1/2}=6.0\,h;E_\gamma=140.5\,keV} {}^{99}Tc$$

One can use either the 740 keV peak of ^{99}Mo or the 140 keV peak of its decay product. Because of the relative values of the half-lives of ^{99}Mo and ^{99m}Tc, after a while radioactive equilibrium between both radionuclides exists. In practice, it is found that equilibrium exists approximately 1 day after the irradiation. Consequently, (1) if the determination of the activity is based on the 740 keV peak, there are practically no limitations for the waiting period, (2) if the determination is based on the 140 keV peak, one should wait for the radioactive equilibrium to be established. This is no inconvenience, on the contrary, it is even recommended to carry out measurements for both peaks, because, in principle, they should lead to values which should be in agreement, thus allowing a check on the internal coherence of the results. In determining the activities, one should pay attention to the standardization of the counting geometry. On the other hand, because one is dealing with measurements over identical peaks, the 740 keV or the 140 keV peaks, it is not necessary to know the efficiency of the detector.

Once the specific activities for each of the samples is obtained, one has to report the activities to the same instant in time and, possibly, to correct for the effect of self-absorption of the gamma-radiation in the samples, particularly if the measurement concerns the lower energy peak.

Finally, the fission interference correction factor, F_{Mo}, is given by the ratio between the standardized specific activities:

$F_{Mo} = A^*_{sp}$ (uranium sample)/A_{sp} (natural molybdenum sample).

Error estimation of the ^{235}U abundance

Equation (3) can be writen as:

$$\theta_{U235} = C_1 F_{Mo} + C_2 \frac{\Phi_{epi}}{\Phi_0} F_{Mo} \qquad (4)$$

where C_1 and C_2 are constants:

$$C_1 = \frac{M_U \theta_{Mo98} \sigma_0}{M_{Mo} y_c g_f \sigma_f} = 2.24 \cdot 10^{-3} \pm 4.9\%$$

$$C_2 = \frac{2 M_U \theta_{Mo98} I}{\sqrt{\pi} M_{Mo} y_c g_f \sigma_f} = 1.34 \cdot 10^{-1} \pm 4.7\%\,.$$

The relative standard errors in C_1 and C_2 are obtained by applying the error propagation law to their respective expressions, taking into account the data in Fig. 1. Note that the error of C_1 is due mainly to the uncertainty in the cross section σ_0 (4.6%), and the error of C_2 is controlled by the uncertainty in the resonance integral I (4.3%).

By applying the error propagation law to Eq. (4), and taking into account the errors of C_1 and C_2, one can estimate the relative error to be expected in θ_{U235}. For that, however, one needs to define the interval of change of Φ_{epi}/Φ_0 and to ascribe a credible error to the values of F_{Mo} and of Φ_{epi}/Φ_0. Usually the NAA experiments are carried out in irradiation facilities where the epithermal to thermal neutron flux ratio is approximately inside the 0.01 to 0.03 interval, (Fig. 1 is a typical example of this situation). Consequently, the $0 \le \Phi_{epi}/\Phi_0 < 0.05$ interval is used here, which is wide enough to meet most of the experimental conditions of practical interest. The typical experimental error in determining the fission interference factor is of about 5% (note that, in Fig. 2, 70% of the experimental values of F_{Mo} fall inside the interval F_{Mo}(calculated) ±5%, approximately). The error associated with Φ_{epi}/Φ_0 depends on the way one uses to determine this parameter. Using the k_0-standardization method, where the ratio $\Phi_0/\Phi_{epi} = f$ is determined directly, it is possible to obtain an uncertainty of about 3%.[18] If the Φ_{epi}/Φ_0 ratio is calculated from the individual neutron flux values Φ_{epi} and Φ_0, the error is probably higher than 3% and depends of course on the corresponding uncertainties (for example, if both the values of Φ_{epi} and Φ_0 are known to be whithin 5%, the error in Φ_{epi}/Φ_0 is about 7%).

According to what was said above, the calculation has been made of the expected error in θ_{U235} for the following conditions (using the $R = \Phi_{epi}/\Phi_0$ shorthand convention): (1) range of R: $0 \le R < 0.05$; (2) error in F_{Mo}: $(\Delta F_{Mo})/F_{Mo} = 5\%$; (3) error in R: $3\% \le (\Delta R)/R \le 7\%$. The results obtained are shown on Fig. 3. One can, therefore, notice that the error in θ_{U235}: (1) is a function of R; (2) is equal to 7% for $R = 0$ (note that this error will be lower if the error in F_{Mo} is lower than 5%); (3) goes through a

minimum for R values which depend on the corresponding error. This type of information can obviously help in optimizing the experimental conditions so as to minimize the error in θ_{U235}. In any case, for the usual experimental conditions and for plausible errors of F_{Mo} and of R, one can conclude that the error to be expected in the θ_{U235} abundance will certainly lie within the range (6±1)%.

Example for the application of the method

The method was applied for determining the abundance of ^{235}U in the uranium of a metallic alloy (1%U-Al), in order to clarify an uncertainty which has arisen concerning the isotopic composition of this material. According to the certificate from the supplier, the uranium in the alloy was supposed to contain 11 ppm of ^{235}U, but, during a study[9] on the dependence of F_{Mo} on the Φ_{epi}/Φ_0 ratio, it became clear that the actual value was very much higher.

Consequently, two distinct ways were used to determine the concentration of ^{235}U in the metallic alloy: (1) using the method suggested in the present work, and (2) using an alpha-spectrometry technique. In the first case, two independent experiments were carried out at irradiation facilities of the Portuguese Research Reactor where the ratio Φ_{epi}/Φ_0 was equal to 0.0120 and 0.0208.

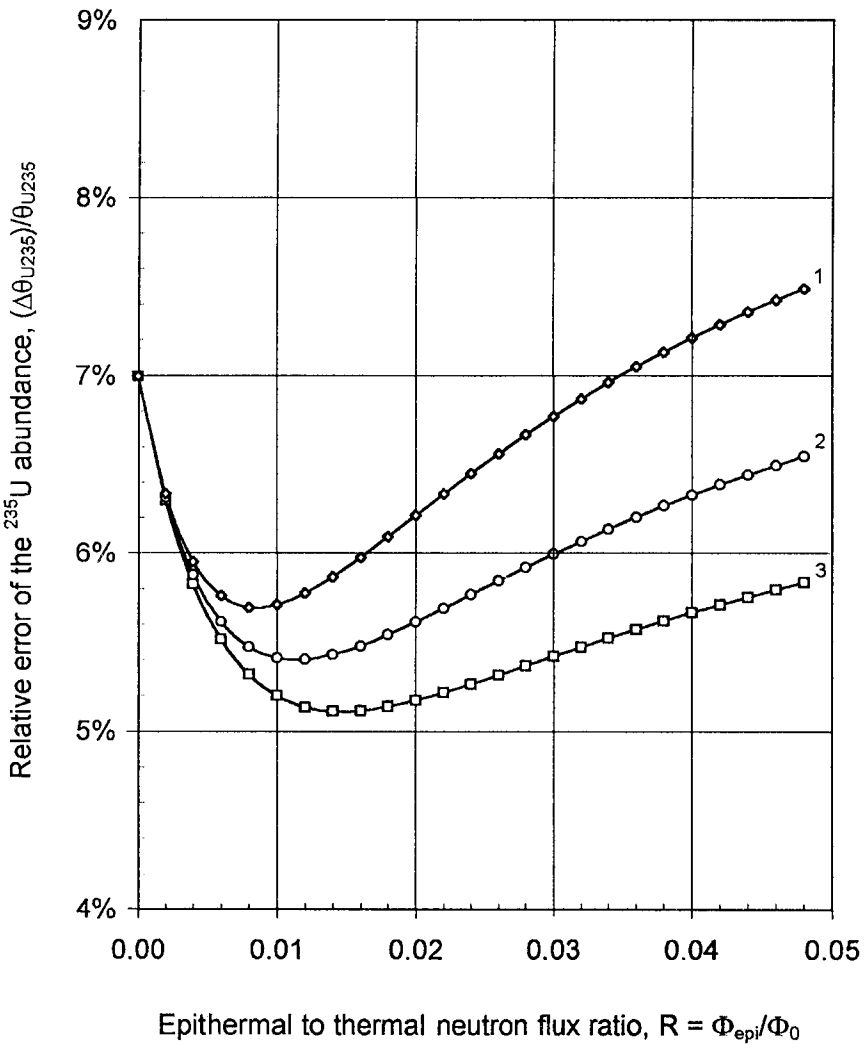

Fig. 3. Expected relative error in the ^{235}U abundance, $(\Delta\theta_{U235})/\theta_{U235}$ (adopted relative errors in F_{Mo} and in $R = \Phi_{epi}/\Phi_0$: $(\Delta F_{Mo})/F_{Mo} = 5\%$, and $3\% \leq (\Delta R)/R \leq 7\%$); error in R, curves: 1–3%; 2–5%; 3–7%

The six values which have been obtained led to the following result: $\theta_{U235} = (3.98 \pm 0.10) \cdot 10^{-2}$ atom % (1σ), which is equivalent to 393±10 ppm. Using the alpha-spectrometry technique, the value obtained for the concentration of ^{235}U was 374±43 ppm (1σ).

Having contacted the supplier of the material, the answer was that, by mistake, the certificate did not correspond to the material and that the value of the concentration of ^{235}U was around $3.8 \cdot 10^2$ ppm.

Conclusions

In certain NAA experiments, the need arises to use natural uranium materials or materials of known isotopic composition. In order to determine the ^{235}U abundance in the uranium which exists in a given material, one may use several analytical techniques, but, NAA being a technique which is currently used in many laboratories, it is interesting to take profit of it to the desired purpose.

In the present paper a method is suggested for determining the ^{235}U abundance in samples of uranium materials. It is an application of the NAA technique based on the determination of the fission interference factor for molybdenum in an irradiation facility where the epithermal to thermal neutron flux ratio may be well known. The method is simple to use, flexible in its application, it does not require ^{235}U certified standards, and it may lead to results with a precision of the order of 6% with one single determination. The repetition of the measurements, preferably by using different irradiation conditions, may allow more precise and exact results to be obtained, as shown in the example of application of the method.

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