J Radioanal Nucl Chem (2017) 311:1453–1458
DOI 10.1007/s10967-016-5105-x

Correction methods for uranium analysis by DNAA

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Received: 22 June 2016 / Published online: 11 November 2016

Abstract Uranium determination by delayed neutron activation analysis is carried out by comparing the delayed neutron counts of a test sample to those of a uranium standard irradiated under identical conditions. Inaccurate results are obtained at high uranium concentrations (greater than approximately 0.05 mg ^{235}U), due to the deterioration of the linear relationship between delayed neutron counts and uranium content, and also when the sample matrix contains other elements that are neutron enhancers or absorbers, for example rare earth elements. In this paper, a correction method has been developed for the accurate analysis of samples with high uranium content (e.g. uranium peroxide). A second correction method, based on the thermal neutron self-shielding calculation developed by Chilian et al., has been applied to DNAA for the first time to correct for neutron absorption interferences in uranium analysis of rare earth-containing samples.

Keywords Delayed neutron · Uranium · Activation · Counting losses · Self-shielding · Rare earth elements

Introduction

Delayed neutron activation analysis (DNAA) is a rapid technique for the accurate determination of uranium in a wide variety of sample types [1]. DNAA is highly sensitive [1, 2] and very precise [2], and uses a relatively large sample size compared with other analytical techniques. DNAA is also non-destructive [1] and can be used routinely to analyse large numbers of samples without requiring sample pre-treatment [2].

The rare earth elements (REE), in particular samarium, europium and gadolinium, are neutron absorbing elements that severely affect uranium analysis by DNAA. Gadolinium is a particularly strong neutron absorber, having a neutron absorption cross-section (49,700 barns), which is significantly larger than that of uranium (7.57 barns) [3].

Much work has been carried out in the literature to develop self-shielding correction methods [4–10]. Recently, Chilian et al. [11, 12] proposed a simple analytical expression for calculating the neutron self-shielding effects in cylindrical samples using both the thermal and epithermal neutron absorption cross-sections of elemental components. The technique was applied to neutron activation analysis (NAA) to correct for self-shielding effects from chlorine [11, 13], bromine [13], iodine [13] and zirconium [12].

At the Australian Nuclear Science and Technology Organisation (ANSTO), there is a need to routinely employ DNAA for the accurate quantification of uranium in a variety of sample types including uranium ores, products and leach residues; uranium-loaded resins and various mineral concentrates. However, methods are not available in DNAA for samples that contain high uranium contents or for those containing high contents of REE. Consequently, in this work, a method has been developed to correct for the delayed neutron counting losses in materials with high uranium, using the delayed neutron emission calculation proposed by Dyer et al. [2]. In addition, the thermal neutron self-shielding correction method developed by Chilian et al. [11, 12] was extended to uranium analysis by DNAA for samples containing REE.

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Table 1 Delayed neutron groups from fission of ^{235}U

Group number	Half-life (s)	Absolute group yield (%)
1	55.72	0.052 ± 1.3%
2	22.72	0.346 ± 1.6%
3	6.22	0.310 ± 3.5%
4	2.30	0.624 ± 5.9%
5	0.61	0.182 ± 6.9%
6	0.23	0.066

Theory

Samples irradiated in a thermal neutron flux result in absorption of a neutron by ^{235}U, forming ^{236}U. The ^{236}U atom undergoes spontaneous fission to produce a number of prompt decay products, some of which remain in highly excited states and decay further by negatron (β^-) emission [2]. These nuclei are known as delayed neutron precursors, since the negatron decay is followed by the instantaneous emission of a delayed neutron for which the half-life coincides with that of its precursor [2]. Table 1 lists the main properties of the six known delayed neutron groups [14] with uncertainties adopted from evaluation of delayed neutron data for the major actinides [15].

Delayed neutron emission can be counted using an array of ^{3}He [1] or BF$_3$ [2, 14] detectors, and is proportional to the ^{235}U content [1, 2]. The ^{235}U concentration is determined by comparing the delayed neutron (measured) count from a test sample with the measured count of a single uranium standard [2], or by using the calibration slope of a series of uranium standards extending over the range of measured counts as shown in Eq. (1) [1].[1] The total uranium concentration is calculated using the isotopic composition of uranium (^{238}U/^{235}U) in the test sample.

$$^{235}\mathrm{U}\ (\mathrm{mg}) = \frac{\text{Measured count of sample}}{\text{Calibration slope}} \quad (1)$$

The comparator method [2] is considered to be an advantage of DNAA because it is simple and rapid; however, the method suffers three main disadvantages. The first is the deterioration of the linear relationship between ^{235}U content and delayed neutrons in samples containing more than 0.05 mg ^{235}U.[2] Second, the assumption is made that the sample and uranium standards interact with neutrons in an identical manner. Finally, the presence of neutron enhancing or neutron absorbing elements in the sample matrix can lead to either the overestimation (enhancers) or underestimation (absorbers) of the delayed neutron counts, and hence the uranium concentration.

Calculation of uncertainties

Uncertainties in the measured counts were calculated from reported uncertainties for the delayed neutron groups from fission of ^{235}U [15]. For all measurements, the calibration slope was determined from a plot of measured counts versus the mass of uranium in the standards. The uncertainties in the detector efficiencies for the high uranium measurements were determined from a plot of measured counts versus the calculated detector efficiencies for high uranium standards. The uncertainties in the self–shielding factor (G_{th}) for the samples containing neutron absorbers were calculated using the Kragten approach, which employs spreadsheet software to calculate the uncertainty of a measurement using an approximate numerical method of differentiation [16, 17]. The method requires knowledge of the calculation used to derive the final result and knowledge of the standard deviations of the individual variable components.

For determination of the uranium concentrations, propagation of uncertainties was utilized by following standard methods [18]. Measurements of separate samples using either the same or a different technique yield independent measurements. The averages and uncertainties of these measurements can be calculated using weighted mean (and associated uncertainty) equations for independent measurements [18].

Experimental

DNAA was carried out at the fully automated irradiation facilities at ANSTO according to an established procedure [19]. Targets were irradiated for 60 s in the 20 MW OPAL research reactor at ANSTO in a stable thermal neutron flux of 5×10^{12} n cm^{-2} s^{-1}. The DNAA irradiation position was located 1.2 m from the reactor core, and the ratio of thermal to epithermal neutron flux was 6700. Targets were counted for 60 s in an array of five BF$_3$ detectors. The detectors had an efficiency of approximately three percent and the delay time between the sample leaving the reactor and the count start time was 16 s. Data were acquired using Siemens Simatic PLC software.

Based on the delayed neutron group data given in Table 1, the delay time before the start of the count (16 s), and a count time of 60 s, the relative contributions to the measured count rate for each of the delayed neutron groups were calculated. Analysis of these data showed that groups one and two predominate. Over the period of the count, group one accounts for 32% and group two for 67% of the total counts. The remaining one percent comes from group three. On the basis of the uncertainties quoted by Rudstem et al. [15], the determined uncertainty in the measured counts is 1.5%.

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[1] Hereafter referred to as the comparator method.

[2] Hereafter referred to as high uranium.

Uranium standards and samples were encapsulated in polyethylene canisters for irradiation, according to an established procedure [20]. Blanks comprised of empty polyethylene irradiation canisters were irradiated at the start and end of each DNAA run. Uranium standards containing up to 35 mg ^{235}U were prepared by evaporation of an accurately weighed quantity of uranium standard solution onto silica.

All of the samples used in the present study originated from natural sources, therefore, ^{235}U and ^{238}U abundances, in accordance with the IUPAC guidelines, were used in all calculations [21].

Results and discussion

Correction method for samples containing high uranium

A disadvantage of DNAA is the deterioration of the linear relationship between ^{235}U concentration and the delayed neutron counts in samples containing more than 0.05 mg ^{235}U, due to increasing counting losses. Consequently, the DNAA comparator method (Eq. (1)) cannot be used to accurately quantify high uranium samples.

In 1962, Dyer et al. published a comprehensive study on the use of delayed neutron counting following neutron activation of ^{235}U [2]. According to Dyer et al., the delayed neutron emission of a fissionable nuclide irradiated with thermal neutrons can be predicted using the equation (Eq. (2)) [2]:

$$N_{\mathrm{d}} = \sigma_{\mathrm{f}}\,\phi\,N \sum \frac{a_{\mathrm{i}}}{\lambda_{\mathrm{i}}}\left(1 - \mathrm{e}^{-\lambda_i t_{\mathrm{b}}}\right) \mathrm{e}^{-\lambda_i t_{\mathrm{d}}} \left(1 - \mathrm{e}^{-\lambda_i t_{\mathrm{c}}}\right) \qquad (2)$$

where N_{d} is the number of delayed neutrons emitted, σ_{f} is the thermal neutron fission cross-section of ^{235}U (cm^2), ϕ is the effective thermal neutron flux (n cm^{-2} s^{-1}), N is the number of atoms of ^{235}U, a_{i} is the absolute group yield of delayed neutron precursors in delayed neutron group i, λ_{i} is the decay constant of delayed neutron group i (s^{-1}), t_{b} is the irradiation time (s), t_{c} is the counting time (s) and t_{d} is the delay time (s).

In this work, the delayed neutron counts (measured counts) of a series of uranium standards containing 0.04–0.35 mg ^{235}U were obtained from irradiation and delayed neutron counting. The expected delayed neutron counts (expected counts) for each of the standards were calculated using Eq. (2) and compared to the measured counts. From this data, the relative detector efficiency for each standard was calculated and then plotted against the measured counts obtained. It was found that the relative detector efficiency decreased linearly with the measured counts (Fig. 1). It can also be seen from Fig. 1 that there is curvature in the data at low measured counts (i.e. at lower ^{235}U concentrations). This is to be expected since at ^{235}U concentrations below 0.05 mg, the relative detector efficiency is invariant. From the equation of the line, the corrected delayed neutron counts (corrected counts) can be calculated using Eq. (3).

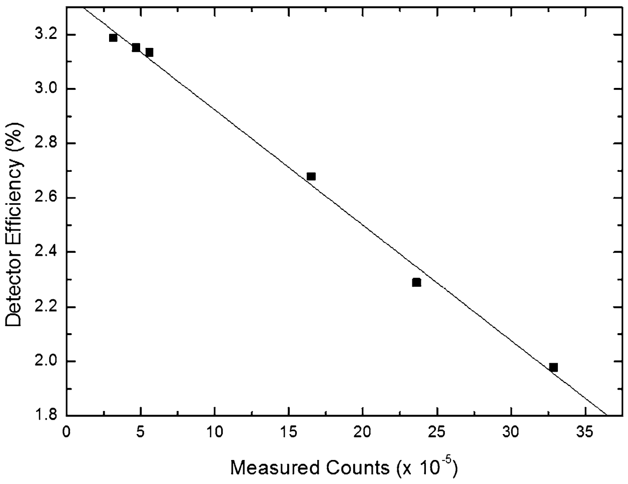

Fig. 1 Measured counts versus relative detector efficiency for uranium standards

$$\text{Corrected counts} = \frac{\text{Measured counts}}{\text{Detector efficiency}} \qquad (3)$$

Two different masses of a single uranium peroxide ($UO_4{\cdot}nH_2O$) sample were irradiated under identical conditions to the uranium standards (test samples, known as ‘UP 1’ and ‘UP 2’). The measured counts were well above the linear range of the comparator method (Eq. (1)) and so the corrected counts were determined as described above (Eq. (3)).

The corrected counts were substituted into Eq. (2) and the respective ^{235}U concentrations calculated. The total uranium concentration was then determined using the natural abundance [21]. The results are shown in Table 2 and are compared to results obtained using the comparator method (Eq. (1)).

The uranium results obtained using the comparator method were inconsistent and showed that as the mass of the irradiated sample increased, the uranium concentration decreased, which was consistent with the decrease in detector efficiency. In contrast, excellent agreement was obtained for the uranium concentration after correcting the measured counts.

The average uranium concentration in the uranium peroxide sample using the correction method was found to be 70.3 ± 0.9 wt% (Table 3). This was in excellent agreement with the average value of 70.4 ± 2.5 wt% (Table 3) obtained for the other analytical techniques. It is also consistent with a well-known form of uranium

Table 2 Results for test samples analysed using the comparator method and the correction method developed in the present work

Sample ID	Mass (mg)	Comparator method		Correction method		
		Measured counts	U concentration (wt%)	Relative detector efficiency%	Corrected counts	U concentration (wt%)
UP 1	28	$1.7 \pm 0.1 \times 10^6$	59 ± 7	2.61 ± 0.01	$6.7 \pm 0.1 \times 10^7$	70.3 ± 1.2
UP 2	57	$2.8 \pm 0.2 \times 10^6$	48 ± 7	2.14 ± 0.01	$1.33 \pm 0.02 \times 10^8$	70.4 ± 1.4

Table 3 Comparison of uranium results obtained by the correction method developed in the present work to other analytical techniques

DNAA (wt%)	Digest/ICPMS[a] (wt%)	Gamma [b] (wt%)	NAA (wt%)	DNAA/Gamma[c] (wt%)	UO_42H_2O
70.3 ± 0.9	73 ± 4	69 ± 7	68 ± 4	71 ± 7	70.4
Average = 70.4 ± 2.5					

Errors presented are for 95% confidence interval based on standard deviation

[a] Sample (0.1 g) dissolved in concentrated nitric acid (5 mL) and made up to 0.1 L

[b] ^{238}U inferred from the ^{234}Th (63.28 keV), ^{234m}Pa (1001 keV) and ^{235}U (185.72 keV) peaks

[c] Gamma counting of the ^{239}Np peaks at 106 and 278 keV in the irradiated DNAA sample

peroxide, $UO_4 \cdot 2H_2O$, which has a uranium concentration of 70.4%.

Correction method for samples containing neutron absorbers

Neutron self-shielding effects in cylindrical samples have been found to be affected by both the thermal and epithermal neutron absorption cross-sections of elemental components [11, 12]. According to Chilian et al., the thermal neutron self-shielding factor (G_{th}) in a cylindrical sample irradiated in a nearly isotropic neutron field is shown in Eq. (4) [11]:

$$G_{th} = \frac{1}{1 + \left(\frac{N_{Av} k_{th}}{r(r+h)} \sum \frac{m_i \sigma_{absi,i}}{M_{at,i}}\right)^{0.964}} \qquad (4)$$

where N_{Av} is Avogadro's number, k_{th} is the thermal self-shielding constant, r and h are the radius and height of the cylinder, respectively (cm), m_i is the amount of element i (g), $\sigma_{abs,i}$ is the thermal neutron absorption cross-section for element i (cm^2) and $M_{at,i}$ is the atomic mass of element i. The thermal self–shielding constant, k_{th}, is an experimentally determined number and Chilian et al. found that the mean measured value of k_{th} was 0.91 at an approximate moderator temperature of 30 °C [11].

In this work, the thermal neutron self-shielding factors for samples containing REE were calculated according to the method of Chilian et al. [11], based on the measured elemental concentrations for the samples. In the OPAL reactor at ANSTO, the thermal to epithermal neutron flux ratio is very large (6700) and the contribution of epithermal neutrons to the overall activation of the target is immeasurably small. Epithermal effects were, therefore, neglected. The mean measured value of k_{th} given by Chilian et al. (0.91) was used in the calculations.

Pressed pellets of a monazite concentrate containing 51 wt% REE (mainly lanthanum, cerium, praseodymium and neodymium), a xenotime concentrate containing 43 wt% REE [mainly yttrium and other heavy REE (terbium to lutetium)] and a rare earth–containing certified reference material, OKA-2 [22] (26% REE) were prepared. A small portion of the sample was mixed with silica and wax (typical ratio 1:3:1, respectively). The radius and height of the pressed pellets were accurately measured and were typically 13 and 2 mm, respectively. Polystyrene foam spacers were placed above and below the sample to centre a pressed pellet inside the polyethylene irradiation canister.

The concentrations of the strongly neutron absorbing rare earth elements samarium, europium and gadolinium in each material are shown in Table 4. Errors in these values were five percent.

The thermal neutron self-shielding factor (shown in Table 5) for each pressed pellet was calculated using Eq. (4) and the full elemental composition of the corresponding REE material (obtained using fusion digest[3]/ICPMS analysis). The self-shielding factor was dependent on the amount of samarium, europium and gadolinium in the pressed pellet, and increased as the concentration of the REE increased. Xenotime had the largest thermal neutron self-shielding factor as it contained the largest concentration of the most strongly neutron absorbing rare earth element, gadolinium.

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[3] Sample (0.1 g) fused with 12:22 lithium tetraborate/metaborate flux (1 g) at 1000 °C and then dissolved in dilute nitric acid [23].

Table 4 Concentrations of elements (±5%) of interest in the monazite and xenotime concentrates, and the OKA-2 standard

Element	Neutron absorption cross-section [4]	Monazite (wt%)	Xenotime (wt%)	OKA-2 (wt%)
Sm	5922	1.3	0.9	0.9
Eu	4530	1.6	0.2	0.2
Gd	49,700	0.8	2.7	0.5

Table 5 Measured and corrected counts and calculated uranium concentrations using the comparator method for monazite and xenotime concentrates and the OKA-2 standard

Sample ID	Uncorrected		Corrected			Reference U concentration (mg kg^{-1})
	Measured counts	Uranium (mg kg^{-1})	Self-shielding factor, G_{th}	Corrected counts	Uranium (mg kg^{-1})	
Monazite						
1	21,245 ± 319	1795 ± 38	0.71 ± 0.01	30,050 ± 687	2573 ± 71	2530 ± 60 (ICPMS)
2	19,852 ± 298	1869 ± 40	0.73 ± 0.01	27,240 ± 597	2599 ± 69	
Average U		1830 ± 28			2586 ± 49	
Xenotime						
1	7754 ± 116	1022 ± 22	0.62 ± 0.02	12,668 ± 190	1694 ± 56	1650 ± 40 (ICPMS)
2	8077 ± 121	988 ± 21	0.61 ± 0.02	13,545 ± 203	1682 ± 57	
Average U		1005 ± 15			1688 ± 40	
OKA-2						
1	1814 ± 27	185 ± 4	0.845 ± 0.008	2156 ± 38	220 ± 5	219 ± 8[a]
2	1887 ± 28	181 ± 4	0.844 ± 0.008	2261 ± 40	216 ± 5	
3	2040 ± 31	176 ± 4	0.825 ± 0.009	2485 ± 46	215 ± 5	
Average U		180 ± 2			217 ± 3	

Errors reported for ‘Average U’ and ICPMS reference values are for 95% confidence interval based on the standard deviation of repeat measurements. Errors for the self-shielding factors were calculated using the Kragten approach

[a] Certified reference value [22]

After irradiating the samples, the measured counts were corrected using the calculated thermal neutron self-shielding factor (Table 5). Since the measured counts were within the linear calibration range for DNAA, the uranium concentration in each sample was determined using the corrected counts and the comparator method (Eq. (1)). The results are presented in Table 5.

Table 5 clearly shows that all samples were affected by self-shielding effects, and therefore, the measured counts significantly underestimated the uranium concentrations. The uranium concentrations for all three samples based on the corrected counts were found to be in excellent agreement with either the certified uranium concentration or the values obtained using fusion digest/ICPMS.

Summary and conclusion

The comparator method is generally considered to be a simple, accurate and rapid means of determining the ^{235}U concentration in samples analysed by DNAA. A major disadvantage of this method is that for samples containing greater than 0.05 mg ^{235}U, delayed neutron counting losses become increasingly significant and affect the linear relationship between delayed neutron counts and uranium content. Additionally, samples containing neutron enhancing and/or neutron absorbing elements interfere with the delayed neutron count from ^{235}U, leading to inaccuracies in the determination of the uranium concentration.

In the present work, a method was developed which corrected for delayed neutron counting losses in samples containing more than 0.05 mg ^{235}U, which allowed the accurate determination of ^{235}U concentrations using the equation proposed by Dyer et al. [2]. A uranium peroxide sample was analysed using this method and was found to contain 70.3 ± 0.9 wt% uranium. This result was in excellent agreement with the average value of 70.4 ± 2.5 wt% obtained from acid digest/ICPMS, gamma spectrometry, NAA and DNAA/gamma spectrometry. The method developed was successfully applied to samples with large uranium concentrations, in this work, up to 70%.

The thermal neutron self-shielding correction method developed by Chilian et al. [11, 12] was used to correct for neutron absorption effects in the certified reference material, OKA-2, and also in monazite and xenotime samples, all of which contained REE, primarily samarium, europium and gadolinium. Based on an extensive literature search, the method of Chilian et al., developed for NAA, has not previously been extended to DNAA. After applying the corrections, the average measured uranium concentration for OKA-2 (217 ± 3 mg kg^{-1}) was in excellent agreement with the certified value of 219 ± 8 mg kg^{-1}. The uranium concentrations for the monazite and xenotime samples were also found to be in excellent agreement with the respective uranium concentrations obtained using fusion digest/ICPMS.

Self-shielding corrections, up to 40%, were carried out for the REE only. Further investigations would need to be carried out to determine if the correction method can be applied for G_{th} values greater than 40%, and also extended to other elemental interferences in DNAA.

Acknowledgements The authors would like to thank Attila Stopic and Paul Brown for providing assistance and advice with this work. Thanks also to Isabella Naletilic, Gordon McOrist, Patrick Yee and Avalin Edisho for providing analytical support.

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