On the accuracy of gamma spectrometric isotope ratio measurements of uranium

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ABSTRACT

The isotopic composition of uranium was measured using high resolution gamma spectrometry. Two acid solutions and two samples in the form of UO_2 pellets were measured. The measurements were done in close geometries, *i.e.* directly on the endcap of the high purity germanium detector (HPGe). Applying no corrections for count losses due to true coincidence summing (TCS) resulted in up to about 40% deviation in the abundance of ^{235}U from the results obtained with mass spectrometry. However, after correction for TCS, excellent agreement was achieved between the results obtained using two different measurement methods, or a certified value. Moreover, after corrections, the fitted relative response curves correlated excellently with simulated responses, for the different geometries, of the HPGe detector.

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1. Introduction

Uranium having different contents of ^{235}U is used in many applications, such as in fuel for nuclear reactors, radiation shielding, and nuclear weapons. Enrichment, or the fraction of ^{235}U, can be measured using different methods, *e.g.* low resolution gamma spectrometry [1], high resolution gamma spectrometry [2,3], mass spectrometry [4], and alpha spectrometry [5]. Gamma spectrometry offers a non-destructive measurement, and can be done on any shape of a uranium sample due to an intrinsic calibration [3]. Using this approach, the measurands, *e.g.* isotope ratios, are fitted by an empirical response function in order to evaluate the isotopic composition [2].

Close geometries, or large solid angles, are often used in gamma spectrometric measurements in order to reduce measurement time, or in order to reduce the minimum detectable activity (MDA), since the efficiency is higher. However, with large effective solid angles, radionuclides emitting gamma photons in cascade will suffer from count losses, due to summation of the gamma photons emitted within the time resolution of the detector system [6–8]. In detectors sensitive to low-energy photons (such as thin-window n-type HPGe detectors), gammas emitted in coincidence with X-rays may also be summed, resulting in coincidence losses (γ–X) [9]. All such count losses, if not corrected for, will result in an underestimation of the determined activity. In fact, peaks may also gain counts due to so called summing in effects. In that case there is a real gamma transition, but also at least two transitions where the sum of the two gamma energies will sum to the peak of the real transition. These kinds of systematic effects have previously not been reported in isotope ratio measurements of uranium.

In this work, the isotopic composition of uranium was measured with gamma spectrometry and with mass spectrometry for comparison. All samples were placed directly on the endcap of the gamma detector, resulting in count losses for some of the gamma lines in the measurement of ^{238}U *via* its daughter ^{234m}Pa. The systematic deviation if these count losses are not accounted for is demonstrated in this work, and furthermore, the results after correction for TCS are reported as well.

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2. Materials and methods

2.1. Theory

The procedure for evaluating the isotopic composition of uranium in gamma spectrometric measurements has been previously presented in the literature [2,3], and will therefore only be presented briefly here. The relative efficiency, $\Psi_{rel,Ej}$, at gamma ray energy E_j can be expressed as

$$\Psi_{rel,Ej} = \frac{C_{i,Ej}}{I_{i,Ej}\lambda_i R_i} \qquad (1)$$

where $C_{i,Ej}$ is the net count rate of a full energy peak at the gamma energy E_j of interest, in this case, the uranium isotope i, $I_{i,Ej}$ the photon emission probability at E_j for isotope i, λ_i the decay constant of the radioactive isotope i, and R_i the isotope ratio of isotope i. In this work, the isotope ratios $^{234}U/^{238}U$ (R_{234}) and $^{235}U/^{238}U$ (R_{235}) were considered. One prerequisite of this method is radioactive equilibrium between ^{234}Th and ^{238}U, which is established after about 200 d. Moreover, a function that describes the detector response is also needed, e.g. [2]

$$\Psi_{rel}(E) = e^{c_1 + c_2/E^2 + c_3 \cdot (\ln E)^2 + c_4 \cdot (\ln E)^3 + c_5/E} \qquad (2)$$

With Eqs. (1) and (2) the isotope ratios of interest can be calculated using a least square method [2,3]. In this work this was done by minimizing the error square sum of the weighted squared differences between the function fit and measurement data. Each measurement data point was weighted by its associated counting statistical uncertainty.

The uncertainty in the parameter estimation, e.g. the isotope ratios, was evaluated by means of the jackknife method [2,10–12], which is a data re-sampling method from which the variance can be calculated as explained in the references.

2.2. Uranium samples

Four uranium samples were measured: three low enriched uranium (LEU) materials, and one natural uranium reference material (IRMM-184). A fraction of one LEU sample was dissolved in nitric acid and measured in a 60 mL plastic container ($d = 62.3$ mm, $H = 19.7$ mm). This geometry was also used for the reference material. Two of the LEU materials were not dissolved, but measured as almost intact UO_2 pellets ($d = 9.1$ mm, $H = 3.5$ mm) having a density of about 10.9 g/cm³.

2.3. Gamma spectrometric measurements

All gamma spectrometric measurements were done using a coaxial p-type high purity germanium detector with an 1.5 mm Al window (HPGe, Canberra, Meridien CT, USA) having a relative efficiency of about 80% ($d = 75$ mm, $L = 75$ mm) and a resolution of about 1.9 keV, both at 1332 keV. The detector was previously modelled in order to facilitate calculation of e.g. different correction factors in gamma spectrometric measurements [13]. The modelled dead layer thickness was 0.60 mm. The detector was shielded using a Canberra 777B ultra low background Pb shield, which is 15 cm thick. Moreover, the sample compartment was continuously flushed with nitrogen gas in order to reduce the background. Using this measurement system, there were no net count rates in the peaks of interest and for the counting times used in this work.

In the evaluation of isotope ratios as measured using gamma spectrometry, the following full-energy gamma ray peaks were used: 120.9 keV (^{234}U); 143.8, 163.4, 185.7 and 205.3 keV (^{235}U); 258.2, 742.8, 766.4, 786.3, and 1001.0 keV (^{238}U via ^{234m}Pa). A small contribution from ^{234}Pa to some of the gamma peaks of ^{234m}Pa was corrected. The measurement times of the samples were long enough

(ranging from about $2.5 \cdot 10^5$–$1.2 \cdot 10^6$ s) to ensure a statistical uncertainty in the individual net peak count rates less than about 0.5%. Maximum count rate (30–2000 keV) was below 800 cps, and the amplifier shaping time was 6 μs. A maximum count rate of about 800 cps can be considered as low enough in order to not result in any significant pile-up effects. Moreover, the percentage dead time in the gamma spectrometric measurements was low, $< 2.5\%$, which ensured no significant random summing (pile-up) during the measurements [14–16]. According to Lindstrom and Fleming [16], the magnitude of pile-up for the shaping time and maximum count rate used in this work would be less than 2%.

Physical data (half-lives and photon emission probabilities) were taken from DDEP (Decay Data Evaluation Project) [17]. Correction factors for true coincidence summing were calculated using EFFTRAN [18], which uses physical data from KORDATEN, and VGSL (Virtual Gamma Spectrometry Laboratory) [19], which uses data from ENSDF (Evaluated Nuclear Structure Data File). In these calculations, the detector, as modelled earlier [13], was implemented in the two codes and used in combination with the geometry of each uranium sample. The two codes handle both self-absorption as well as differences in geometries relative to the geometry used in the detector modelling.

The two samples measured as UO_2 pellets were almost intact. Only very small pieces were missing. However, for the calculations of correction factors these samples were approximated as being cylindrical. All samples were placed directly and centred on the endcap of the HPGe detector.

2.4. Determination of isotope ratios using ICP-SFMS

The instrumentation used for the mass spectrometric measurements of samples 1–3 was an ICP-SFMS (Element XR, Thermo, Bremen, Germany) in low resolution mode.

For tuning of the ICP-MS a tuning solution, ICP Multi-element standard solution Certipur XXIII (Merck Millipore, Darmstadt, Germany), was used to obtain maximum uranium intensity whilst keeping the uranium oxide formation as low as possible. The automatic dead time correction was disconnected as this correction was performed post-acquisition. All standard solutions and samples were diluted to appropriate concentrations using MQ water (Merck Millipore, Darmstadt, Germany) and concentrated nitric acid (for analysis EMSURE, Merck, Darmstadt, Germany, further purified in-house by sub-boiling distillation in a quartz still).

For the determination of uranium, the instrument was calibrated for mass bias using the reference material IRMM-073/1 (IRMM, Institute for Reference Materials and Measurements, Geel, Belgium).

The raw data were extracted from the instrument and data reduction thereafter was done off-line in order to correct detector dead time of the individual, averaged signal intensities according to the non-paralysable detector model [20].

The detector dead time, τ, and its associated uncertainty, was previously determined to 32.85(83) ns, with the 70 ns nominal dead time setting on the ion detection board using IRMM-073/3, -073/5 and -073/7 (IRMM, Institute for Reference Materials and Measurements, Geel, Belgium) via a ratio-based determination described by Appelblad and Baxter [21].

Following the dead time correction, the intensities were corrected for contributions from blank levels, and thereafter mass bias corrected ratios were calculated using the Russell equation [22]. To determine the isotope amount ratios in the samples, the samples were diluted in order to achieve signals for ^{234}U, ^{235}U and ^{238}U within the range of the counting detector, i.e., below $5 \cdot 10^6$ counts per second.

All uncertainties were evaluated in accordance with ISO/GUM [23] using the software GUM Workbench [24]. All uncertainties are