

Intercalibrated radionuclide activities in spiked water samples of the IAEA worldwide open proficiency test

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Abstract Proficiency testing is one of methods for regularly assessing the accuracy of the analytical data produced by laboratories for particular measurements. In 2008 and 2010, we participated in the IAEA 2008 and 2010 worldwide open proficiency tests on the determination of natural radionuclides in water spiked with ^{226}Ra , ^{234}U and ^{238}U for activity analysis and with ^{90}Sr and ^{230}Th for gross alpha/beta analysis. Feedback statistics from the IAEA final report showed that the radioactivities of all of the samples fell within an acceptable range according to the IAEA. For ^{226}Ra analysis, our result showed that ^{229}Th – ^{225}Ra is suitable as a chemical tracer, although there are doubts that different co-precipitation efficient between parent ^{229}Th and its daughter nuclide ^{225}Ra in published literature. The impact factors of the analysis results, such as the lower limit of detection, standard substances, the background and efficiency for daily determination, are discussed in detail.

Keywords Radionuclide · IAEA · Water · Proficiency test · Intercalibration

Introduction

A proficiency test (PT) is one of the series of activities organised every year by the IAEA terrestrial environment laboratory, and testing is one of the important ways for evaluating the accuracy of daily analytical procedures and final results from research laboratories. The accuracy of

analytical data plays an important role not only in our research activities but also in our daily lives in fields, such as environmental protection, international trade, law enforcement and consumer health. In addition, measurements performed by laboratories located around the world should yield traceable and comparable results [1–3]. Therefore, frequent participation in international proficiency tests can identify the analytical problems of laboratories.

Based on IAEA experience with open worldwide laboratory intercomparison studies, a modified *u*-score evaluation and *z*-scores are applied in determining a laboratory's performance, in which the trueness and precision of participants' results are evaluated separately. In this approach, both accuracy and precision have to be 'acceptable' for the final results to also be acceptable. Otherwise, the reported results are 'not acceptable'. Such an estimation approach for each set of reported results can identify not only methodological problems affecting accuracy but also shortcomings in uncertainty estimation [1, 4].

According to IAEA's evaluation report [1], the initial step in evaluating a score for the reported data is estimating the bias of each laboratory. The relative bias (RB%) between the reported value (each laboratory, A_{lab}) and the given value by IAEA (A_{ref}) can be calculated by

$$\text{RB\%} = \frac{A_{\text{lab}} - A_{\text{ref}}}{A_{\text{ref}}} \times 100\% \quad (1)$$

The 'trueness' of the reported results will be determined to be 'acceptable' if the values of activities in final report can be as

$$A_1 \leq A_2 \quad (2)$$

A_1 as

$$A_1 = |A_{\text{ref}} - A_{\text{lab}}| \quad (3)$$

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and A_2 as

$$A_2 = 2.58 \times \sqrt{\text{Unc}_{\text{ref}}^2 + \text{Unc}_{\text{lab}}^2} \quad (4)$$

where A_{ref} and A_{lab} are the activities of each nuclide given by the IAEA (traceable from NIST) and lab analysis, respectively. Unc_{ref} and Unc_{lab} are concerned with uncertain error.

Participants' results are scored as 'acceptable' for precision when ($P < \text{LAP}$) or ($P = \text{LAP}$). For evaluation of precision, estimator P is calculated for each participant with the following formula:

$$P = \sqrt{\left(\frac{\text{Unc}_{\text{ref}}}{A_{\text{ref}}}\right)^2 + \left(\frac{\text{Unc}_{\text{lab}}}{A_{\text{lab}}}\right)^2} \times 100\% \quad (5)$$

P is directly obtained from the reported measurement uncertainty by each laboratory. Based on the concentration or activity level of each nuclide and the complexity of the analytical problem, the acceptance limit for precision (LAP) for each nuclide is differently defined as showed in Table 1 [1, 5].

The estimation results of gross alpha/beta activities in the spiked water were applied using R (= Lab value/Lab uncertainty) and RB. More details are available for reference in the report by Shakhshiro et al. [1].

Experimental

The sample was prepared using tap water outsourced in one batch from Seibersdorf laboratories and then was spiked with an appropriate amount of radionuclide solution [1].

For Ra analysis, 10 dpm ^{229}Th – ^{225}Ra tracer (code 6229, Eckert & Ziegler) was inserted into a 20 g spiked water sample after acidifying with HNO_3 . Here, we assume that the recoveries of radium and thorium from the sample were equal, as much of the original ^{225}Ra decayed before further steps were completed. $\text{Pb}(\text{NO}_3)_2$ solution was added to the acidic sample to form a $\text{Pb}(\text{Ra})\text{SO}_4$ co-precipitation by adding dilute H_2SO_4 and solid K_2SO_4 . The co-precipitate was centrifuged and redissolved in ethylene diamine tetraacetic acid (EDTA). This solution was passed through an anion exchange column (DOWEX 1X8-200, 100–200 mesh, chloride form, 50 mm height, 7 mm i.d.) and a cation exchange column (DOWEX 50WX8-200, 200–400 mesh, 80 mm height, 7 mm i.d.). Finally, Ra isotopes were electrodeposited onto a stainless steel disc and determined by alpha-spectrometry (Model: Canberra 7200-08). The activity of ^{226}Ra was obtained immediately after the counting [6].

Similarly, a ^{232}U tracer (code 7432, Eckert & Ziegler) was added into 30 g spiked water after acidifying the sample for $^{234,238}\text{U}$ analysis. The water was converted to a

9 mol/L HCl solution and then loaded onto a resin column (DOWEX 1X8-200, 100–200 mesh, chloride form, 80 mm height, 7 mm i.d.). Uranium was then eluted using 0.1 mol/L HCl. Finally, uranium was electrodeposited onto a stainless steel disc. After electrodeposition onto stainless steel discs, the activity of uranium was determined by alpha-spectrometry.

For gross alpha/beta activity, analyses are referenced as reported by Zhang et al. [7]. Briefly, the radioactivity of gross alpha and gross beta were determined with a MPC 9604 ultra-low-level counter, while U_3O_8 (which was fired from $\text{UO}_2(\text{NO}_3)_2$ and KCl) was selected as sub-standard and standard reference substances.

Results and discussions

First, we used 500 mL water sample to determine whether activities in the spiked water can be quantified by He-gamma spectrometry. The one typical gamma-ray spectrum is showed in Fig. 1, which shows that there are almost no gamma-ray peaks after counting for 12 h. Generally, ^{226}Ra and $^{234,238}\text{U}$ or their daughter nuclides below 1 Bq/kg in water are difficult to quantify by gamma-ray spectroscopy because of a lower limit of detection (LLD) that is mostly caused by low detection efficiency due to the background contribution. Furthermore, ^{238}U lacks direct gamma emissions and can be measured only assuming a radioactive equilibrium with the daughter nuclide ^{234}Th (useful gamma emissions at 63.3 and 92.4–92.8 keV); ^{226}Ra has a direct gamma emission at 186.2 keV strongly interfering with both ^{235}U gamma emission and the background contribution [8–10].

As Table 1 shows, the laboratory has a good intercalibration result using α -spectroscopy. For ^{234}U and ^{238}U , most A_1 values were much lower than A_2 values, and P values were also much lower than LAP. For ^{226}Ra , A_1 values were just a little lower than A_2 values. The absolute value of relative bias ranged from 1.79 to 39.76%, and most of the relative bias values were lower than 15% (Fig. 2). All of the lab values were acceptable, except one ^{226}Ra value (because of the calculating mistake).

As IAEA reported [1], there are 32 and 36 laboratories that had only one or two 'not acceptable' results, respectively. The unacceptable performance was mainly due to ^{226}Ra .

Because the analytical system is a complex system, such cases can even include human factors, cultural effects and the specific conditions of each laboratory that can impact intercalibration results. Therefore, it is quite normal to make some mistakes in an analytical laboratory. However, their impact on the analysis data should be noted.

Table 1 The results for the intercalibration sample and for the laboratory [5]

| | IAEA value (Bq/kg) | IAEA Unc (Bq/kg) | No. of reported results | Percentage of 'acceptable' (%) | Percentage of 'warning' (%) | Percentage of 'not acceptable' (%) | Lab value (Bq/kg) | Lab Unc (Bq/kg) | Rel. bias. (%) | A ₁ | A ₂ | P (%) | Final score | | |
|-----------------|--------------------|-------------------|-------------------------|--------------------------------|-----------------------------|------------------------------------|-------------------|-----------------|----------------|----------------|----------------|-------|-------------|----------------|---|
| IAEA-CU-2008-03 | Sample-1 | ²²⁶ Ra | 0.69 | 0.04 | 125 | 48 | 8 | 44 | 0.55 | 0.08 | 23.19 | 0.16 | 0.23 | 11.05 | A |
| | | ²³⁴ U | 0.56 | 0.02 | 107 | 66 | 7 | 26 | 0.57 | 0.02 | 1.79 | 0.01 | 0.07 | 5.01 | A |
| | | ²³⁸ U | 0.36 | 0.01 | 125 | 56 | 10 | 34 | 0.37 | 0.02 | 2.78 | 0.01 | 0.06 | 6.08 | A |
| | Sample-2 | ²²⁶ Ra | 1.93 | 0.09 | 136 | 54 | 7 | 39 | 1.83 | 0.19 | -5.18 | 0.10 | 0.54 | 11.38 | A |
| | | ²³⁴ U | 1.2 | 0.04 | 108 | 63 | 10 | 27 | 1.08 | 0.16 | -10.00 | 0.12 | 0.43 | 15.19 | W |
| | | ²³⁸ U | 1.25 | 0.04 | 129 | 56 | 9 | 36 | 1.11 | 0.07 | -11.20 | 0.14 | 0.21 | 7.07 | A |
| | Sample-3 | Gross alpha | <0.2 | | 124 | 88 | 2 | 10 | 0.11 | 0.16 | | | | | A |
| | | Gross beta | <0.3 | | 125 | 82 | 6 | 13 | 0.07 | 0.65 | | | | | A |
| | Sample-4 | Gross alpha | 3.93 | 0.08 | 136 | 60 | 21 | 19 | 3.83 | 0.53 | -2.54 | | | | A |
| | | Gross beta | 15.7 | 0.3 | 143 | 75 | 18 | 7 | 13.3 | 0.5 | -15.29 | | | | A |
| Sample-5 | Gross alpha | 7.68 | 0.15 | 138 | 67 | 15 | 18 | 8.3 | 1.4 | 8.07 | | | | A | |
| | Gross beta | 30.7 | 0.6 | 142 | 83 | 10 | 7 | 29.3 | 1.2 | -4.56 | | | | A | |
| IAEA-CU-2010-03 | Sample-1 | ²²⁶ Ra | 0.04 | | | | | 0.05 | 0.006 | | | | | A | |
| | | ²³⁴ U | 0.04 | | | | | - | | | | | | A | |
| | | ²³⁸ U | 0.04 | | | | | - | | | | | | A | |
| | Sample-2 | ²²⁶ Ra | 0.86 | 0.02 | | | | 0.93 | 0.04 | 8.14 | 0.07 | 0.12 | 4.89 | A | |
| | | ²³⁴ U | 1.3 | 0.03 | | | | 1.18 | 0.06 | -9.23 | 0.12 | 0.17 | 5.58 | A | |
| | | ²³⁸ U | 0.7 | 0.02 | | | | 0.66 | 0.03 | -5.71 | 0.04 | 0.09 | 5.37 | A | |
| | Sample-3 | ²²⁶ Ra | 1.57 | 0.04 | | | | 0.52 | 0.01 | -66.88 | 1.05 | 0.11 | 3.19 | N ^a | |
| | | ²³⁴ U | 0.47 | 0.01 | | | | 0.46 | 0.03 | -2.13 | 0.01 | 0.08 | 6.86 | A | |
| | | ²³⁸ U | 0.31 | 0.01 | | | | 0.28 | 0.02 | -9.68 | 0.03 | 0.06 | 7.84 | A | |
| | Sample-4 | Gross alpha | 4.8 | 0.1 | | | | 4.04 | 0.43 | -15.83 | | | | A | |
| | Gross beta | 9.1 | 0.2 | | | | 8.99 | 0.24 | -1.21 | | | | A | | |
| Sample-5 | Gross alpha | 8.5 | 0.2 | | | | 11.88 | 2.17 | 39.76 | | | | A | | |
| | Gross beta | 11.1 | 0.3 | | | | 12.35 | 0.37 | 11.26 | | | | A | | |

^a The 'not acceptable' result was caused by calculating mistake

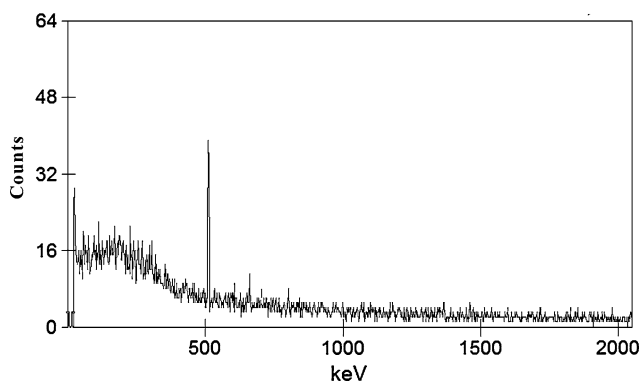
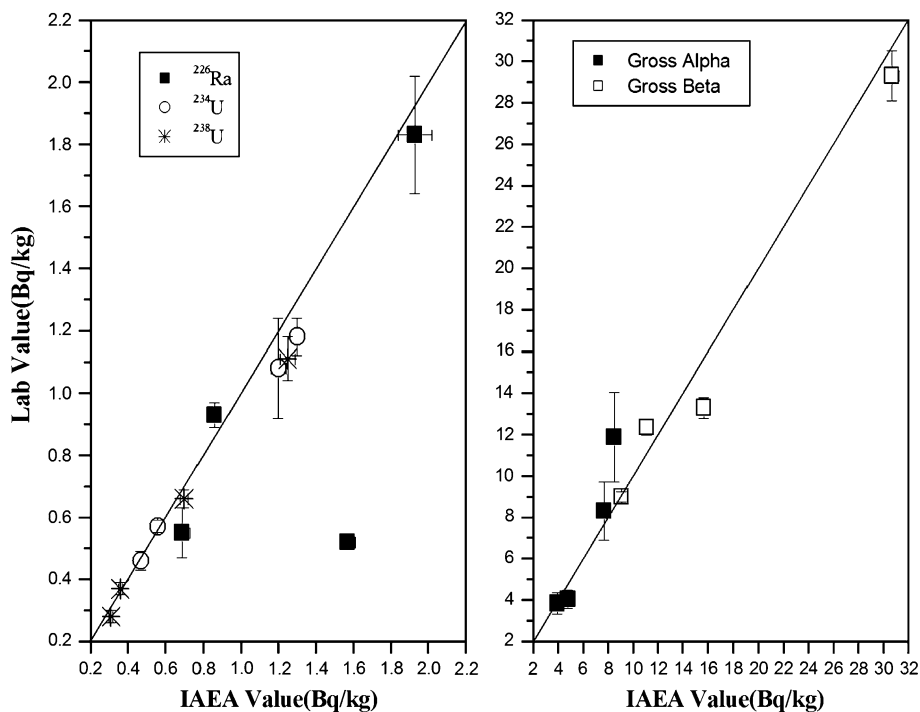


Fig. 1 The gamma-spectroscopy of water sample-1 of IAEA-CU-2010-03

Tracer choice

Because of the complex radiochemical procedures for the analyses of ^{226}Ra , ^{234}U and ^{238}U , yield tracers are necessary. The choice of yield tracer is important in an analysis to distinguish chemical recovery between the tracer and the nuclides. For the ^{226}Ra measurement, the normal tracers are ^{225}Ra , ^{224}Ra , ^{223}Ra and ^{133}Ba [11–15]. Benedik et al. [14] showed that the activity concentrations of ^{226}Ra are within measurement uncertainties for ^{225}Ra , ^{223}Ra , and ^{133}Ba . A lower recovery was always found when ^{133}Ba was used. ^{223}Ra and ^{225}Ra are generally used, but due to their short half-lives, their decays should be taken into account as well as the growth of their decay products.

Fig. 2 A comparison of the laboratory results with the IAEA value



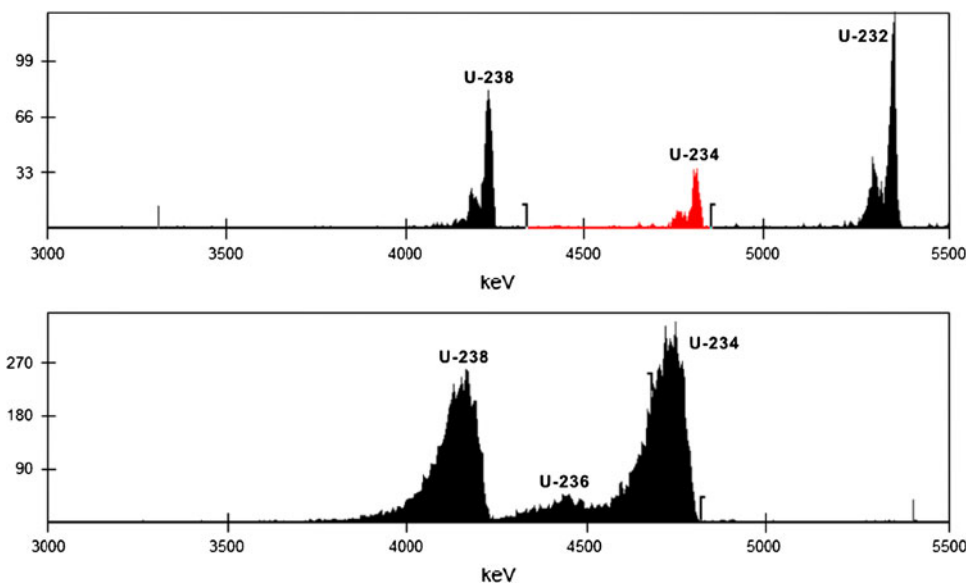
For ^{234}U and ^{238}U measurement, ^{232}U and ^{236}U are widely used [16–22]. It is necessary to distinguish between the tracer and the nuclides. ^{232}U and ^{236}U can both be used as tracers for the measurement of uranium (Fig. 3). Figure 3 shows that the distance between ^{232}U and ^{234}U or ^{238}U is larger than the distance between ^{236}U and ^{234}U or ^{238}U . Therefore, ^{232}U is better for tracer yield, especially when the chemical operation has some problems and the background and the tail of the peak is high.

U_3O_8 and KCl were selected as sub-standard and standard reference substances for gross alpha analysis and gross beta analysis, respectively. The results indicate that when one selects $\text{UO}_2(\text{NO}_3)_2$ as a sub-standard reference substance for gross α analysis, the total alpha activity of $\text{UO}_2(\text{NO}_3)_2$ is much lower than that of the standard U_3O_8 that is recommended by GB 5750-85, only because the ^{238}U and ^{234}U do not reach the secular equilibrium for our laboratory sub-standard $\text{UO}_2(\text{NO}_3)_2$ reagent. However, no effect of such $\text{UO}_2(\text{NO}_3)_2$ on the analysis of gross alpha activity was observed after the activity of ^{234}U and ^{238}U was qualitatively measured by alpha-spectrometry.

Detector background

The background of alpha-spectrometry is very low in comparison with the background of gamma-spectrometry, as the system is a vacuum system. However, the background is important for the analysis of gross alpha and gross beta, especially when the environmental sample's activity is small. The capacity of the detector is an important factor for

Fig. 3 The spectrum of uranium measurement using ²³²U and ²³⁶U as tracers



the background, such as the lead block, the air and the tray. The filter is usually used in environmental sample analysis, and the material of the filter can greatly affect the background. The difference between various materials is too high as showed in Table 2. It can be seen that the background of the QMA filter (Whatman) is the highest, and the backgrounds of the acetate (Xinya), mixed cellulose ester (Xinya) and nuclear track membranes (Whatman) are almost the

same. These results are comparable with the results reported by Ma et al. [23]. In addition, the results in Table 2 show that the background with and without air circulation in the instrument room did not change much. This result indicates that the air does not affect the background of the detector.

The background is related to the LLD and can be estimated as follows [24, 25]:

$$LLD = \frac{4.66\sqrt{B}}{\eta mt} \times 100\% \tag{6}$$

where *B* is the background counting number, η is the fractional counting efficiency, *m* is the sample mass, and *t* is the count time. For the analysis of environmental samples, the LLD should reduce the background, promote detectable efficiency and extend the detection time.

For the alpha-spectrometry vacuum, the background of alpha-spectrometry can be neglected. However, for gross alpha and gross beta procedures, the background is one of the most important factors. The background of trays without sample was detected for calculating the lower limit of detection. The change in the lower limit of detection (5 g sample) with the detected time was shown in Fig. 4. Figure 4 indicates that LLD decreased with the detected time. The LLD decreased sharply within 240 min, but the LLD did not change greatly after 240 min. For the environment sample, which has low activity, the LLD should be detected within at least 4–5 h.

Shape and tail of the peak in alpha-spectroscopy

As many environmental samples have relatively low count rates for alpha-spectroscopy, the extent of the tailing of alpha peaks of lower energy is a critical factor for accurate spectral analysis.

Table 2 The background of the detector and the filters

| Material | Sample number | Net count rate (cpm) | Average net count rate (cpm) |
|--|---------------|----------------------|------------------------------|
| Background of detector (with air circulation) | | | 0.46 ± 0.06 |
| Background of detector (without air circulation) | | | 0.48 ± 0.02 |
| QMA filter (Whatman) | GF-1 | 2.553 | 2.36 ± 0.29 |
| | GF-2 | 2.031 | |
| | GF-3 | 2.495 | |
| QMA filter (Xinya) | GF-5 | 1.024 | 1.07 ± 0.03 |
| | GF-6 | 1.101 | |
| | GF-7 | 1.075 | |
| | GF-8 | 1.067 | |
| Cellulose acetate membranes (Xinya) | CA-1 | 0.024 | 0.08 ± 0.08 |
| | CA-2 | 0.027 | |
| | CA-3 | 0.179 | |
| Mixed cellulose ester (Xinya) | MCE-1 | 0.019 | 0.05 ± 0.03 |
| | MCE-2 | 0.094 | |
| | MCE-3 | 0.033 | |
| | MCE-4 | 0.037 | |
| Nuclear track membranes (Whatman) | NT-1 | 0.046 | 0.046 ± 0.001 |
| | NT-2 | 0.047 | |

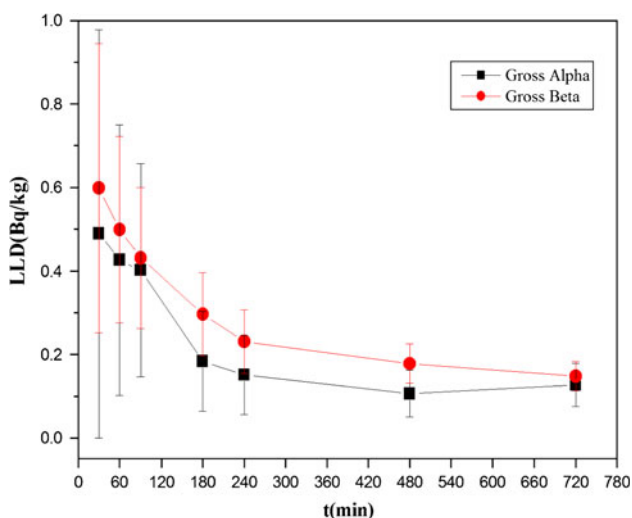


Fig. 4 The LLD of gross alpha/beta vs. detected time (the background count number was the background of trays without sample and the mass was assumed to be 5.00 g)

The chamber gas pressure and source deposit thickness are the main factors affecting the tailing and peak resolution. Martin and Hancock [26] reported that full width at half maximum (FWHM) increased linearly with mass per unit area. Although the measurement has a procedure to separate the impurities, the sample may still have some impurities during the environmental sample analysis, and the deposit source may be thick. The unproficient operation can also have a thicker deposit source.

Estimated error of the results

In the final evaluation, both sources for trueness and precision were combined. The measurement uncertainty was used for calculating the trueness and precision, which are important for improving the measurement uncertainty. The laboratories' results show that much of their uncertainty is higher than the IAEA's uncertainty, which may influence the results.

The uncertainty in the measurement activity of gross alpha can be calculated using the equation [7]:

$$S = C \cdot \sqrt{\left(\frac{S_{m_s}}{m_s}\right)^2 + \left(\frac{S_m}{m}\right)^2 + \left(\frac{\sqrt{S_{n_x}^2 + S_{n_0}^2}}{n_x - n_0}\right)^2 + \left(\frac{\sqrt{S_{n_s}^2 + S_{n_x}^2}}{n_s - n_x}\right)^2} \tag{7}$$

The uncertainty of the measurement activity of ²²⁶Ra, ²³⁴U, ²³⁸U and gross beta can be calculated as the following equation:

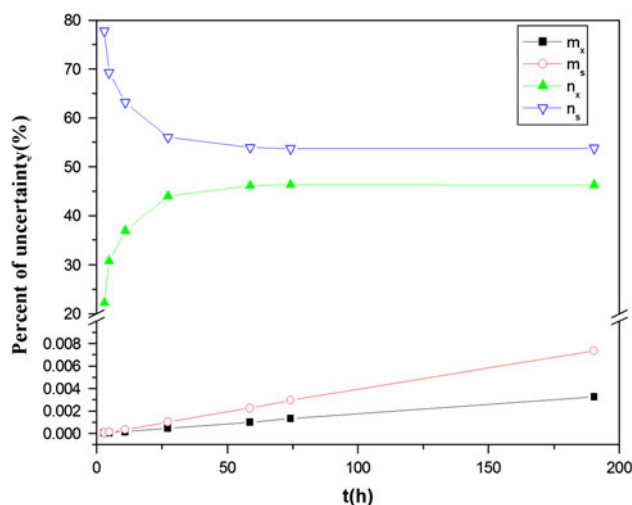


Fig. 5 The percent of each part in calculating the measured uncertainty vs. the detected time (30.00 g sample-3 of IAEA-CU-2010-03 with 2.000 dpm ²³²U tracer)

$$S = C \cdot \sqrt{\left(\frac{S_{m_s}}{m_s}\right)^2 + \left(\frac{S_m}{m}\right)^2 + \left(\frac{\sqrt{S_{n_x}^2 + S_{n_0}^2}}{n_x - n_0}\right)^2 + \left(\frac{\sqrt{S_{n_s}^2 + S_{n_x}^2}}{n_s - n_x}\right)^2} \tag{8}$$

where m_s and m are the mass of the standard solution and the mass of the sample; n_x , n_0 and n_s are the count rate of the sample, background and standard solution; S_{m_s} and S_m are the uncertainty of the mass of the standard solution and the mass of the sample; and S_{n_x} , S_{n_0} and S_{n_s} are the uncertainties in the sample count rate, background and standard solution.

Figure 5 shows the percentage of each part of the uncertainty in measured ²³⁸U activity with detected time. The results indicate that the uncertainty of the mass of the standard solution and of the sample accounted for only a small percentage of the uncertainty (less than 0.001%). The uncertainty of the mass of the standard solution and the sample is specific to a laboratory, and it can be reduced with as much sample as possible. The uncertainty in the measurement activity is most dependent on the uncertainty in the count rate. The sum of the uncertainties in the count rate of a sample and the standard solution can reach almost 100%. The percent of the uncertainty in the count rate of a sample increased with the detection time, and the percent of the uncertainty in the count rate of the standard solution decreased within 25 h. After 25 h, the percent of the uncertainty in the count rate of the sample and the standard solution were comparable. However, the uncertainty in the count rate decreased exponentially over time. To improve

the precision, suitable materials and a suitable environment should be selected to reduce the background. A sample should be detected for as long as possible to obtain a reasonable measure of uncertainty in the count rate.

Conclusions

Although the analytical system is a very complex system, good results can be obtained when care is taken with impact factors such as background and the environmental conditions of each laboratory.

Generally, proper equipment, human resources and material resources are important factors in obtaining reliable and high-quality results. Further improvement in the radiochemical analytical procedures for the determination of natural and transuranic radionuclides at a low level of radioactivity is necessary by capacity building with such analytical procedures.

To reduce the background and the lower limit of detection, the choice of a suitable material should be taken into account, especially when the activity is low. More samples and an extended analysis time can lower the uncertainty in measure activities.

Certain recommendations from the IAEA report can definitely enhance the analytical performance of the participating laboratories. In the present work, some comments and recommendations are given below.

The determination of chemical yield is also a limiting factor for the determination of radium and uranium isotopes by alpha-spectrometry. In the case of Ra, there are assumptions about its equilibrium, both with parent (^{229}Th) and daughter (^{225}Ac) nuclides. Although uranium measurement by alpha-spectrometry is a well-established procedure, it is not the easiest method. Moreover, special care should be taken to avoid cross-contamination from the repeated use of beakers and deposition cells. The internal yield tracers must be assured at all times once opened (and diluted), and internal procedures should be applied for their management (dilutions included), possibly including periodical monitoring of their actual concentrations.

The gross alpha/beta measurements are considered to be primarily screening determinations. Radionuclides were successfully used in calibrations, including ^{40}K and $^{238}\text{U}/^{234}\text{U}$.

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