

Preparation of in-house calibration source for the use in radioactivity analysis of the environmental samples: consideration of homogeneity

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Abstract An in-house reference material has been prepared in Kuwait Institute for Scientific Research radioecology laboratory, for quality control purposes of gamma spectrometer systems. The material contains a known amount of uranium ore reference material (prepared by the International Atomic Energy Agency and coded as IAEA-RGU-1) which is mixed with marine sediment collected from Kuwait bay. The IAEA-RGU-1 has been certified that it is in equilibrium state with the decay daughters, and stable to be used for quality control purposes. Nevertheless, the homogeneous distribution of the doped material with the prepared source should be verified. This has been examined using gamma spectrometry measurements in conjunction with analysis of variance statistical tools, Dixon, box plots and Grubbs tests. The calculated total uncertainty has been utilized to establish the recommended specific activity ranges of ^{226}Ra , ^{224}Th , ^{214}Pb , ^{214}Bi and ^{210}Pb radioisotopes in the prepared source. The obtained results showed that the estimated uncertainty arising from the sample inhomogeneity has a significant contribution in the total uncertainty. The stability control charts of the ultra-low background gamma spectrometry system demonstrated the suitability of the prepared material for the purpose of quality control. However, the emitted gamma-rays from the prepared source covers the required energy range for determination of natural and artificial radionuclides in different species of environmental samples such as marine sediment, soil samples, and samples contaminated by naturally occurring radioactive material produced by oil

industry. In addition, the material might be used for system calibration in case its traceability is proven. The experimental data revealed the significance of the homogeneity in preparing environmental samples for radioactivity measurements; in particular when small sample quantities of environmental samples are required to be analyzed.

Keywords Gamma spectrometry · Sediment samples · In-house preparation calibration sources · Quality control material · Homogeneity testing

Introduction

Certified reference materials (CRMs), as well as reference materials (RMs) play a major role in the analytical measurements of laboratories to attain valid analytical results that support important decisions in the fields of health, environment, transportation and international trade [1]. They are regularly used, e.g., on a daily basis for the purposes of calibration, evaluation of measurement uncertainty and quality control purposes.

There are four groups of RMs recognized by the international organization for standards ISO guide 30 [2]. One group includes primary standards (PS), that are widely accepted as having the highest metrological qualities, and whose values are accepted without reference to other standards of the same quantity. A second group (secondary standards (SS)) have documented values relative to the PS. The third group of CRMs have one or more characteristics certified by an analytical procedure to establish traceability. CRMs values are usually accompanied by an uncertainty for a stated confidence level. The last category is the RMs in which one or more of whose property values are sufficiently homogeneous and well established to be used

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for the calibration of an apparatus, the assessment of a measurement method, or assigning values to materials. However, it should be stressed that the ISO guide 30 currently is under revision, and the new definition of RMs as acknowledged by ISO REMCO [3] pointed out that the use of RMs might include the calibration of measurement systems and quality control. The new definition has also stressed that a RM can only be used for a single purpose in a given measurement, i.e. a single measurement of RM cannot be simultaneously used for calibration and quality control. This conception of limiting the use of RMs has been clearly specified by the IAEA publications and certification reports [4]. Furthermore, CRMs and RMs might be used in testing the measurement systems, calibration and evaluation of analytical performance of the laboratories and the analysts, in addition to adapting the analytical methods and assessing the measurement's uncertainty [5].

In general, the use of CRMs on a routine basis in the working of the analytical laboratory is very expensive. The alternative is to prepare an in-house RMs by following the internationally recognized guidelines, such as, the ISO guide's procedures for the preparation of RMs [6]. It should be emphasized that in-house RMs do not replace the CRMs; instead, they provide an inexpensive and cost effective material for maintaining the quality of the analytical results by keeping the laboratory under strict statistical control. However, unlike the CRMs, in-house RMs do not have to be fully traceable standards. This limits their use for quality control purposes which is a major part of the laboratory quality assurance program. Therefore, the intended use of the RMs should be specified in the initial stage of preparation, i.e. either for quality control or for calibration purposes; but not for both.

The use of the calibration source in this work was limited for quality control purposes of gamma spectrometry systems available in KISR's radioecology laboratory, although, the suitability of the prepared source for calibration of the gamma spectrometry system has been examined.

Two major factors have to be fulfilling in case the calibration source is designed for quality control purposes, i.e. stability and homogeneity. So far, the experience gained with the IAEA RMs, including the IAEA-RGU-1, showed that these materials are quite stable and therefore very suitable for quality control purposes. Nevertheless, the problem of the homogeneity assessment associated with the preparation of in-house calibration sources has to be investigated. It becomes critical, especially when diluting solid RMs, similar to the IAEA-RGU-1, with a solid matrix (e.g. powder, granules, etc.). Therefore, developing an approach for testing the homogeneity of the prepared calibration source is extremely important.

On the other hand, the conformity of the source traceability and estimating the total uncertainty has to be considered in

case the calibration source is designed for calibration purposes. However, the suitability of the prepared source for calibration of the gamma spectrometry system has been examined. This has required assigning the recommended ranges of the specific activity of the existing radionuclides, i.e. ^{214}Pb ; ^{214}Bi , ^{226}Ra , ^{234}Th and ^{210}Pb . Statistical tools for instance ANOVA and box plot outliers' detection tests were applied to estimate the total uncertainty. However, the components of the total uncertainties consist of two components, i.e. the uncertainty arising from the preparation process as well as the uncertainty associated with the statistical radioactivity measurement.

Practically, the prepared material was exploited to make calibration sources in different counting geometries for controlling the sample analysis. This is considered necessary for the laboratories dealing with different types and quantities of various environmental samples. However, the determination of the radioactive contents of various natural and anthropogenic radionuclides of interest is required in favor of environmental monitoring. In addition, special radionuclides such as ^{137}Cs , ^7Be and ^{210}Pb have found extensive applications related to estimation of sediment accumulation rates and soil erosion [7–9]. Therefore, such preparation becomes vital in view of the fact that the emitted gamma-rays from the prepared sample covers the energy range required for quantitative determination of the above mentioned radionuclides, which adds more value to the prepared RM.

Methods and measurements

Sample collection and preparation

Core sediment was collected from a site located near the South-East Boubyan Island in the Arabian Gulf at a depth of about 10 m. The total sample was dried in an oven for 48 h at 90 °C, then milled after the removal of large gravel and the remnants of herbal plant materials and double sieved through 90 μm mesh stainless steel sieve. The sample was then placed in a three-dimensional mixer for 24 h. Subsequently, the sediment sample was equally divided into two portions each about 500 g; the first portion saved as a blank sample; while the second was doped with the uranium ore RM. An amount of 100 g of the IAEA-RGU-1 containing 4.97 Bq g^{-1} of natural uranium in equilibrium state was added [10]. The combination was packed in a 2-l container, sealed and placed in a three-dimensional mixer for 48 h. The mixture was then divided into 16 equally weighted subsamples and placed in small petri-dish (30 g in each dish). Gamma spectra for three randomly chosen subsamples, have been collected for preliminary estimation of the mixture homogeneity before

proceeding with the preparation procedure. The count rate of ^{210}Pb and ^{234}Th gamma line was calculated in each sample spectrum to make sure that the mixture was initially homogeneous i.e. the coefficient of variance between the replicates was less than 5 %. After the preliminary homogeneity test passed, the 16 petri-dishes were tightly sealed and stored for about a month to attain secular equilibrium between ^{222}Rn and its daughters, ^{214}Bi and ^{214}Pb . This step is critical since the final homogeneity depends on observing the count rates of ^{210}Pb and ^{234}Th , in addition to the gamma lines of ^{214}Bi and ^{214}Pb .

It should be noted that all staff involved in this process has been following the necessary appropriate radiation protection precautions when dealing with the IAEA-RGU-1 RM.

Homogeneity testing

There are several factors that usually cause difficulty in determining the activity of gamma-emitters in solid samples by gamma spectrometry. These include the counting geometry, measurement system stability, and homogeneity of the measured sample and the standard calibration source. The homogeneity is the most complex factor, since the other factors are typically related to the measurement system's adjustment and that can be controlled. Therefore, it is a crucial need to ensure that the homogeneity of the prepared sample fits for the analysis purpose. To accomplish this goal, the gamma spectrometry method was used to observe the photo-peak intensities of the selected samples for homogeneity testing. The number of the samples required for this test was calculated according to a formula presented in a British Standard on methods for sampling and chemical products BS5309 part 1 [6]. The following formula was used to calculate the number of units required to study the homogeneity

$$\text{Number of units} = 3(\sqrt[3]{n}) \quad (1)$$

where n is the total unit of the prepared sample, which is, in our case, 16 U 30 g each. Based on that, seven samples (groups) were randomly chosen for homogeneity testing. Each sample was repeatedly analyzed six times using the ultra low background (ULB) gamma spectrometry system for a counting time of 10,000 s that led to acceptable statistical intensities of the ^{214}Pb , ^{214}Bi , ^{226}Ra , ^{234}Th and ^{210}Pb photo-peaks. The radioactivity of the above mentioned radioisotopes was calculated in accordance with the characteristic of the spectral lines listed in (Table 1). Dixon and Grubbs statistical outliers' tests in conjunction with ANOVA technique were applied to the analytical results. However, it is usually necessary to establish homogeneity both between and within the individual groups in case the matrix of the prepared material is solid [11]. So that, the

Table 1 Gamma spectral lines and the relative intensities used in the gamma spectrum analysis (updated data by the Laboratoire National Henri Becquerel, http://www.nucleide.org/DDEP_WG/DDEPdata.htm)

Radionuclide	Energy (keV)	Yield (%)
^{210}Pb	46.5	4.25
^{234}Th	63.3	3.75
^{214}Pb	295.2	18.41
	351.9	35.6
^{214}Bi	609.3	45.49
	1120.3	14.91
	1764.5	15.31

variances of the mean squares within and between the groups were used to calculate the F critical value in order to estimate the significance level of these variations. The comparison of the calculated F critical value with the one obtained from the theoretical F distribution is estimating to what extent the sample is considered homogeneous. In addition, the output parameters of the ANOVA statistics were utilized in documenting the recommended specific activity of the prepared sample, in addition to evaluating the total uncertainty. However, the box plot explanatory data analysis tool [12] was used to easily detect the outliers by means of graphically characterizing the experimental data, e.g. distribution, non-outlier range, mean, median, and upper and lower quartiles.

Several guidelines exist for the preparation and homogeneity testing of RMs [13–15].

Gamma spectrometric measurement and analysis

A high resolution gamma spectrometry system, with a background reduction capability, was used to analyze the samples selected for homogeneity testing. The system is equipped with a high purity germanium (HPGe) planar detector of 5,000 mm² surface area. The detector end-cap is enclosed with a thin low background carbon epoxy entrance window for resolving low gamma energies with excellent resolution, i.e. the full width at half maximum (FWHM) at 122 keV is 700 eV. The detector was linked to a high performance spectroscopy workstation of an 8 K multichannel analyzer and controlled by Canberra Genie-2000 gamma acquisition and analysis software. The essential characteristic of this spectroscopic system is the effective and appropriate shielding design that assists in the determination of natural and man-made radioisotopes, including sources of low-energy gamma radiation, with very low detectable activity. The passive shielding is coupled with an active anti-cosmic veto shelter that enhances the capabilities of the passive shield with respect to the suppression of background secondary cosmic rays.

Detailed technical specifications about background reduction can be found in the works of Schwaiger et al. [16] and D. MrYa et al. [17] papers.

The detector efficiency was calibrated using a certified gamma mixed standard solution covering the energy range from 30 to 3 MeV. The standard solution was prepared by Deutscher Kalibrierdienst (DKD), Germany, and it was claimed that the product complies with the requirements for traceability to National Institute of Standards and Technology (NIST) specified in the American National Standards. However, the correction for cascade summing was performed by the Genie 2000 analysis software. This correction is extremely important when determining the specific activities of the free cascade summing radioisotopes.

The specific activities of ^{214}Pb , ^{214}Bi , ^{226}Ra , ^{234}Th , and ^{210}Pb radioisotopes were determined by analyzing the collected gamma spectra using the spectral lines presented in (Table 1). It should be noted that indirect determination of ^{226}Ra activity was estimated based on the weighted average activity for the most intense gamma lines of ^{214}Bi and ^{214}Pb . This arrangement eliminates the uncertainty caused by the interference of ^{235}U gamma line when it is directly determined through the major gamma line (186.2 keV) of ^{226}Ra .

Results and discussion

Homogeneity test result

Results of Dixon and Grubbs tests are shown in (Table 2). It is demonstrated that in all cases, the largest calculated test figure is less than their respective tabulated values at 95 % significant level, providing that the data set is free of outliers. The box and whisker plot of the data distribution shown in (Fig. 1) confirmed this observation, otherwise; symbols indicating outliers and extremes will be presented above or lower the non-outlier range. However, the combination of these statistical tests demonstrated the homogeneity of the prepared sample, i.e. the supplementary

Table 2 Outliers test results for sample homogeneity testing

Radionuclide	Dixon test ^a	Grubbs test ^b	<i>F</i> value ^c	
			Calculated	Calculated
^{210}Pb	>0.36	>0.81	1.25	0.300
^{234}Th	>0.41	>0.59	1.06	0.400
^{214}Pb	>0.33	>1.09	4.47	0.002
^{214}Bi	>0.01	>0.42	1.14	0.370
^{226}Ra	>0.10	>0.90	3.66	0.006

^a Dixon critical *Z* value for $n = 7$ is 0.507

^b Grubbs critical value *Q* for $n = 7$ is 2.02

^c ANOVA *F* critical value for $n = 7$ is 2.37

uranium ore is distributed or diluted homogeneously in the filling material (sediment). In other words, all samples of the same weight contain the same radioactivity concentration, leading to the conclusion that they are drawn from a population with the same average. On the other hand, ANOVA calculates the variance between and within samples, i.e. variance between the replicates per group, as well as the dispersion among the seven groups. The latter reflects the sample preparation such as inhomogeneity and different masses and densities; while the variance between replicates is affected by measurement parameters such as counting statistics, the effect of source to detector geometry, background variations, electronics noise and detector response stability. However, both parameters were utilized to calculate the *F* and *P* coefficients which were used as an indicator for decision: at what level is the prepared sample considered homogeneous?

According to (Table 2), it becomes apparent that the *F* value of ^{226}Ra and ^{214}Pb exceeds the theoretical *F* critical value, indicating that the material is not homogeneous at 95 % confidence level. These abnormal values can be explained by the attribution factors affecting the ^{214}Pb measurement and not the prepared material since the test results of the other isotopes passed the test. It should be noted that the abnormal *F* value of ^{226}Ra is due to the contribution of ^{214}Pb since it was calculated by the weighted mean of the ^{214}Pb and ^{214}Bi gamma lines. Nevertheless, in either case where the calculated *F* value is smaller or larger than the *F* critical value, the uncertainty associated with sample preparation should be evaluated.

Documenting radioactivity recommended values and estimating the total uncertainty

Documenting the recommended values of the prepared sample and evaluating the overall uncertainty for a specific

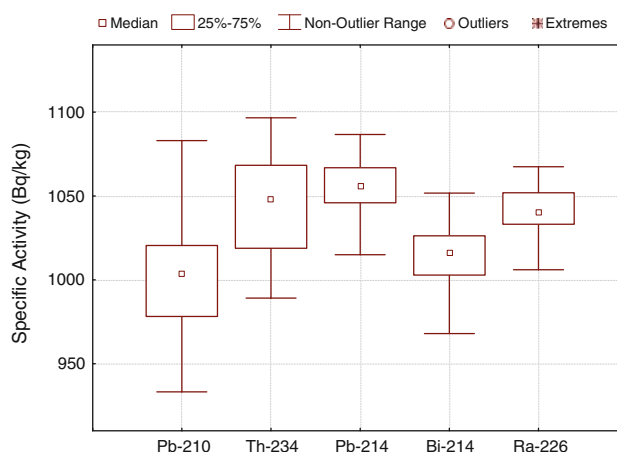


Fig. 1 Box-plot of the specific activities for different radioisotopes in the prepared sample

degree of confidence is extremely critical. The statistical results of the replicates have been used to document the specific activity of ²¹⁴Pb, ²¹⁴Bi, ²²⁶Ra, ²³⁴Th and ²¹⁰Pb in a dry weight unit, and to calculate the total uncertainty for 95 % confidence level. The specific activity was described by the statistical mean and the interval range for a certain degree of confidence as shown in the formula below:

$$\bar{X} \pm \left(t * \frac{S}{\sqrt{n}} \right) \tag{2}$$

where \bar{X} is the average of all repeated measurements, i.e. the pooled average of the seven groups measured six times repetitively. The term $\left(t * \frac{S}{\sqrt{n}} \right)$ is the measurement range at 95 % confidence limit, or the confidence interval, S is the standard deviation of all replicates which in our case is 42, n is the number of replicates in each group which equals six, and t is a student factor for six replicates at 95 % confidence level.

The uncertainty estimation of \bar{X} was determined assuming that the source of the total uncertainty consists of two components: the measurement and the inhomogeneity uncertainties. Therefore, the total uncertainty U_{tot} can be statistically described by the following formula [13]:

$$(U_{tot})^2 = (U_{meas})^2 + (U_{mat})^2 \tag{3}$$

where U_{meas} refers to the statistical measurement uncertainty of the specific activity, and U_{mat} is the uncertainty arising from the sample inhomogeneity. However, the U_{meas} comprises the uncertainty related to the measurement system, e.g. the sample to detector geometry effect, measuring system response the counting efficiency, gamma line intensities and background interference. While the uncertainty arising from sample inhomogeneity was calculated in terms of the total uncertainty:

$$(U_{mat})^2 = (U_{tot})^2 - (U_{meas})^2 \tag{4}$$

where (U_{tot}) can be expressed in the form of:

$$U_{tot} = t_{(pn-1)} S_{tot} \tag{5}$$

where P is the number of test samples or test groups (7) and S_{tot} is the total standard deviation, which is described by the formula:

$$S_{tot} = \sqrt{\frac{u - \frac{(\sum_1^p a_i)^2}{pn}}{pn - 1}} \tag{6}$$

where a_i is the sum of the readings of i group and u is the sum of squares of all measurements.

The recommended values of the radionuclide specific activity in the prepared sample and the associated uncertainties are shown in (Table 3). As noted from the table, the uncertainty attributable to the sample inhomogeneity was found to be about 1.8 times of the statistical measurement uncertainty, which points out the importance of estimating this uncertainty component when preparing a sample for calibration or quality control purposes. Additionally, the large magnitude of this component indicates the significance of the sample preparation by reaching a certain level of homogeneity, especially when preparing environmental samples for radioactivity determination.

Efficiency calibration

The counting efficiency of the measurement system was established using the recommended specific activities with the associated total uncertainty as shown in (Fig. 2). It should be noted that the peak efficiency calculation was based on the net peak area, i.e. the background contribution of the filling material (sediment) has been subtracted. The calculated efficiency was utilized to determine the specific activity of a CRM IAEA 447 Moss-soil [18]. This arrangement is considered necessary to ensure the validity of the preparation procedure. It should be noted that, cascade summing correction for the gamma lines of ²¹⁴Pb and ²¹⁴Bi has been applied when determination of free cascade summing radioisotopes are required such as ¹³⁷Cs, ⁴⁰K and ²⁴¹Am in the Moss-soil sample.

The obtained results were compared with the IAEA certified values and presented in (Table 4). The calculated relative biases (the percentage variations between the laboratory measurements and IAEA certified values) indicating that all results are comparable; provided that the prepared calibration source is generating valid results. It should emphasize that the radioactivity determination of ²¹⁰Pb, ²³⁴Th and ²⁴¹Am is critical by gamma spectrometry

Table 3 The recommended values and the associated uncertainties of the radionuclide concentration in the prepared sample

Radionuclide	Mean (Bq kg ⁻¹)	U_{tot} (Bq kg ⁻¹)	U_{meas} (Bq kg ⁻¹)	U_{mat} (Bq kg ⁻¹)	Total uncertainty (%)
²¹⁰ Pb	1003	66.5	32.7	57.9	6.6
²³⁴ Th	1046	54.4	26.7	47.4	5.2
²¹⁴ Pb	1056	32	15.5	27.5	3.0
²¹⁴ Bi	1015	38.2	18.8	33.2	3.8
²²⁶ Ra	1042	29.6	14.5	25.7	2.8

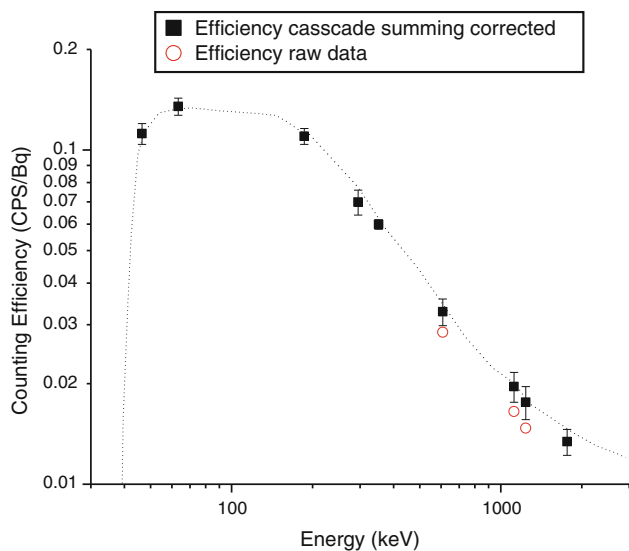


Fig. 2 The counting efficiency curve of the prepared sample with corrected and uncorrected cascade summing

analytical method due to the effect of self absorption at low energy of the gamma spectrum. Therefore, a precise estimation of the counting efficiency at low energy is required. However, the obtained results of these radionuclides were in good agreement with the certified values which adds more value to the prepared calibration source.

Quality control

An imperative purpose of the prepared calibration source was to continuously verify the analytical procedure and hence to maintain the quality of the laboratory. This is being carried out by analyzing the prepared calibration source along with each batch of samples. Besides, the source was used on weekly bases to test the stability of the spectrometry system. Figure 3 shows the quality control chart of ^{210}Pb concentration with acceptable, warning and action limits criteria, i.e. the mean, two and three standard

deviations respectively. The quality control chart of ^{210}Pb specific activity was used to ensure the stability of the measurement system and the validity of the results being generated. In addition, the calibration source was also used to monitor the noise level and the detector resolution by generating quality control charts of the FWHM at low and high energies. FWHM quality control charts of gamma lines 46 and 1,120 keV have been generated as shown in Figs. 4 and 5 respectively. More quality control procedures can be developed using the prepared sample in order to maintain the quality of the data generated by the laboratory. This can be carried out either by controlling the measuring system or by continually assessing the performance of the analyst.

Conclusions and recommendations

The preparation of an in-house calibration source containing an accurate amount of uranium ore RM was described. Gamma spectrometry measurements in conjunction with statistical analysis were applied to determine the level of residual inhomogeneity. This approach was found helpful in estimating the total uncertainty associated with the assigned recommended specific activities of ^{214}Pb , ^{214}Bi , ^{226}Ra , ^{234}Th and ^{210}Pb radionuclides. The statistical analysis of the experimental data revealed the importance of the homogeneous sample; where the uncertainty arising from the material homogeneity might exceed the measurement uncertainty. This becomes considerable in particular, when analyzing small quantities of environmental samples.

The validity of the preparation procedure and the suitability of the calibration source for the analysis fit of purpose were tested by means of cross calibration checking. The comparison of the analysis results of the IAEA Moss- soil RM were in agreement with the IAEA certified values for the radionuclides exist. Nevertheless, if the intention was to use the in-house calibration sources for the

Table 4 The comparison results of the IAEA 447 reference sample

Radioisotope	Lab. value (Bq kg ⁻¹)	Lab. uncertainty (Bq kg ⁻¹)	IAEA value (Bq kg ⁻¹)	IAEA uncertainty (Bq kg ⁻¹)	Relative bias (%)
^{210}Pb	438	29	424	20	3.3
^{234}Th	26.8	2.5	25.5	3	5.1
^{241}Am	2.38	0.22	2.2	0.2	8.2
^{212}Pb	35.2	1.2	37	1.5	-4.9
^{228}Ac	33.9	2	37	2	-8.4
^{214}Pb	23.6	1	26	2	-9.2
^{208}Tl	11.9	0.7	13	0.5	-8.5
^{214}Bi	22.4	1	24.8	2	-9.7
^{137}Cs	427	17	425	10	0.5
^{40}K	544	21	550	20	-1.1

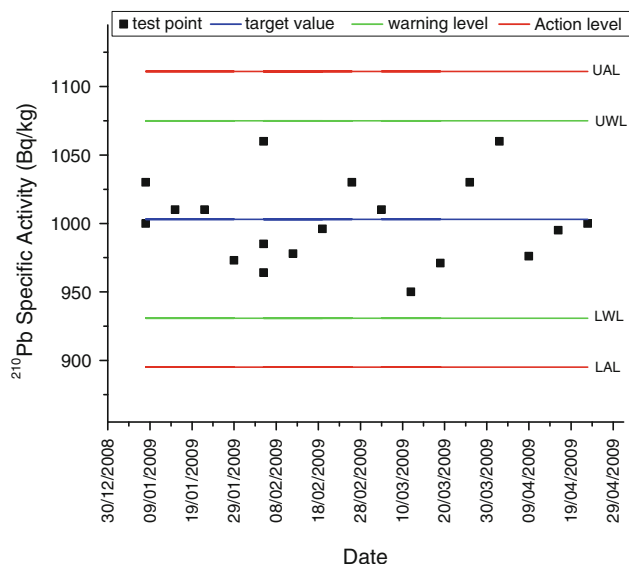


Fig. 3 Stability quality control chart of the ULB gamma spectrometry system using the prepared calibration material

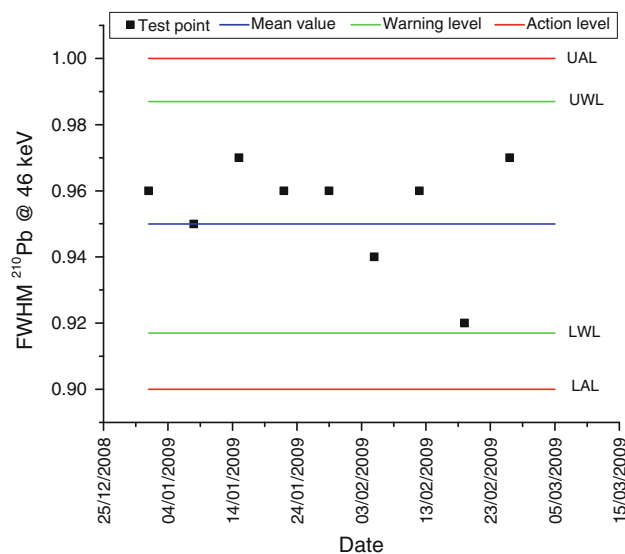


Fig. 4 Quality control chart of FWHM at 46 keV of the ULB gamma spectrometry system using the prepared calibration material

calibration purposes, a requirement is to fully confirm the metrological traceability of the assigned values. This goal is challenging and hard to fulfill by most of the laboratories performing routine analysis. In this context, the quality control charts of gamma spectrometry stability generated by the prepared calibration source, demonstrated that this material is considered appropriate for the purpose of laboratory quality control. Finally, using the uranium ore as a doped material has two major advantages, firstly, it covers the energy range of the most important natural and man-made radionuclide of concern in environmental protection, and secondly, the long half life of uranium (4.9×10^9

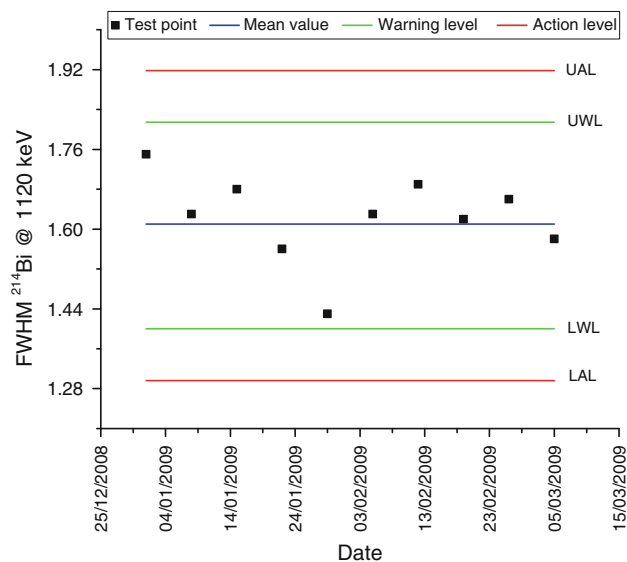


Fig. 5 Quality control chart of the ULB gamma spectrometry system resolution using the prepared calibration material

years) makes it possible to use the prepared source for extended periods without any restriction.

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References

1. Guidelines for the selection and use of reference materials, ILAC-G9:2005 (2005)
2. ISO Guide 30:1992, Terms and definitions used in connection with reference materials
3. Emons H, Fajgelj A, van der Veen A, Watters R (2006) Accred Qual Assur 10:576–578
4. IAEA-TECDOC-1350 (2003) Development and use of reference materials and quality control materials. ISBN 92-0-103303-6
5. Sill CW, Sill DS (1995) Solid standards for quality control in radiochemical analysis. Radioact Radiochem 6(2):28–39
6. Brian B (1998) Guidelines for the in-house production of reference material, LGC/VAN/1998/090
7. He Q, Walling DE (1996) Use of fallout Pb-210 to investigate long-term rates and patterns of over-bank sediment deposition on the floodplains of lowland rivers. Earth Surf Process Landf 21:141–154
8. Appleby PG, Oldfield F (1992) Application of lead-210 to sedimentation studies. In: Ivanovich M, Harman RS (eds) Uranium-series disequilibrium: application to earth, marine and environmental sciences. Clarendon Press, Oxford, pp 731–738
9. Al-Masri MS, Aba A, Khalil H, Al-Hares Z (2002) Sedimentation rates and pollution history of dried lake: Al-Oteibeh Lake. Sci Total Environ 293(2002):177–189
10. Preparation of gamma-ray spectrometry reference materials RGU-1, RGTh-1, and RGK-1 Report-IAEA/RL/146, Vienna (1987)

11. Walker R, Bedson P, Lawn R, Barwick VJ, Burke S, Roper P (2001) Applications of reference materials in analytical chemistry. ISBN: 978-1-84755-938-8
12. McGill RJ, Tukey W, Lagsen W (1978) Variations of box plots. *Am Stat* 32(1):12–16
13. Biagini R, Dersch R, de Felice P, Jerome SM, Perkin EME, Pona C, de Sanoit J, Woods MJ (1995) Homogeneity testing of spiked reference materials. *Sci Total Environ* 173(174):267–274
14. Sahuquillo A, Bosch H, Rauret G, Muntau H (1998) Certified reference materials for extractable trace metals in soils, effect of the particle size. *Fresenius J Anal Chem* 360:304–307
15. Keamer GN, Muntan H, Maier E, Pauwels J (1998) The production of powdered candidate biological environmental reference material in the laboratories of the Joint Research Center. *Fresenius J Anal Chem* 360:299–303
16. Schwaiger M, Steger F, Schroettner T, Schmitzer C (2002) A ultra low level laboratory for nuclear test ban measurements. *Appl Radiat Isot* 56(2002):375–378
17. MrYa D, Bikit I, Žikić-Todorović N, Forkapić S, Slivka J, Vesković M (2007) First tests of the active shield for a gamma ray spectrometer. *Radiat Meas* 42(2007):1361–1367
18. IAEA-447, Natural and artificial radionuclides in moss-soil. <http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Radionuclides/IAEA-447.htm>. Accessed 18 Oct 2011