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A statistical method for the assessment of metrological characteristics of reference materials

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Abstract

Standard reference materials of the composition and properties of substances and materials are used in both industrial and non-industrial sectors of society to ensure measurement uniformity and traceability in those types of measurements that cannot be provided using standards.

During times of war and increased nuclear threat due to a full-scale invasion by an aggressor state, there is a need for heightened attention to the verification of ionizing radiation detection blocks, measurement channels of radiation monitoring systems, radiometers, and radiometric installations, as well as alpha, beta, and gamma radiation spectrometers.

The aim of the paper is to demonstrate the method to evaluate the measurement uncertainty of reference materials (Europium-152 (Eu-152), Caesium-137 (Cs-137), and Thorium-232 (Th-232)) when they are generated and calibrated according to the international regulations. The evaluation of the measurement uncertainty of a radioactive reference material with a natural half-life period is relevant and valid, considering its homogeneity properties and stability. To assess the properties, as well as the measurement uncertainty, one-variant variance analysis was performed.

Keywords: radiation control; reference materials; homogeneity properties; stability; measurement uncertainty; metrological characteristics.

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Introduction

Evaluation of the metrological characteristics of reference materials is one of the important stages of work during the development and release from production of batches or copies of standard samples. In the National Standards on Radiation Safety of Ukraine, the permitted levels of the intake of a radionuclide by the organs of the respiratory system, as well as its permitted concentrations in the open air at operating premises, are specified [1].

The creation of reference materials of Eu-152, Cs-137, and Th-232 is driven by the need for their application during the verification of legislatively regulated measuring instruments used for assessing radiation doses to the population, radiation hygiene monitoring, and continuous control of radiation safety parameters.

Eu-152 is used for calibrating gamma spectroscopic installations that are used for remote measurements of building materials and food products.

State sanitary norms establish permissible levels of radionuclide content, including Cs-137 (along with Srontium-90), in food products and drinking water. The operation of nuclear power plants is the primary sources of the intake of radionuclides of Cesium-137 into the ecosystem.

Th-232 is the most common radionuclide found in building materials, along with Radium-226 and Potassium-40. It is Th-232 specifically that is monitored in building materials during the reconstruction of residential and industrial structures that were destroyed during the war.

The assessment of homogeneity properties is required in case of a batch calibration so that an adequate level of homogeneity of samples of the batch is maintained [1, 2].

The assessment of stability properties is required to establish the instability degree of the original reference materials (RMs) as soon as they are prepared or to verify the continued stability of the material, considering its natural half-life. Even so-called "stable" materials can actually show some instabilities for one or more than one parameter [3].

According to the paper topic, the homogeneity properties and stability of the materials with the

Table 1

Materials for investigation

Radionuclide	Weight, g	Activity, Bq·kg^{-1}
Eu-152	1000	6990
Cs-137	1000	2000
Th-232	1500	2850

radionuclides of Eu-152, Cs-137 and Th-232 shall be estimated (see Table 1).

Assessment of material homogeneity

For samples, being homogeneous is important to guarantee that for each property the same values are demonstrated by a sample of each RM; the homogeneity is also essential if users divide the sample material into some parts (subsamples).

Hypothetically, it is considered that a material is totally homogeneous against specific activities when there are no distinctions in the characteristic values if we compare, for example, two samples. Nonetheless, when it comes to practice, it is considered that a material is homogeneous against a given parameter if the characteristic values of two samples are not exactly the obtained component of the measurement uncertainty, for instance, resulting from estimations.

For particular purposes, the homogeneity properties and stability inherent in the source of a radionuclide and its certain behaviour patterns (when the weight of a material demonstrating a specific activity (6990 Bq·kg^{-1}, 2000 Bq·kg^{-1}, 2850 Bq·kg^{-1}, respectively) is divided into several parts), are assessed according to DSTU ISO 17034:2020. The overall number of materials for testing, the fragments that contain Eu-152, Cs-137 and Th-232, is partitioned by the quartering technique into 20 individual parts of 50 grams each (75 grams for Th-232). Fig. 1 shows the parts that contain the material.

The homogeneity properties and stability were studied for the most common behaviour patterns when verifying legal measuring instruments. Moreover, the behaviour of 6990 Bq·kg^{-1} (for Eu-152) is harmless in terms of the workload on the detector of gamma spectrometer and, which is most crucial, on the personnel [4].

To measure the activity of the overall material number as well as the material in individual parts, the gamma-spectrometric method is used to further determine the composition of nuclides, and Marinelli beakers of the capacity that suits best. Fig. 2 shows the Marinelli beakers to measure the material activity undergoing the test.

The homogeneity results for the materials that contain Eu-152, Cs-137 and Th-232 are shown in Table 2. For further calculations, we determine the average value of each of the 20 portions of materials.

A SEG-002 "AKP-P" gamma radiation energy spectrometer was used to study the specific activity (Fig. 3). In Table 3, the metrological characteristics are provided.

Fig. 1. Dividing the overall number of material into portions (individual parts)

Fig. 2. Marinelli beaker

Fig. 3. General appearance SEG-002 "AKP-P"

Table 2

Test materials. The results of measurements

Portions	Result 1, kBq			Result 2, kBq			Result 3, kBq		
	Eu-152	Cs-137	Th-232	Eu-152	Cs-137	Th-232	Eu-152	Cs-137	Th-232
1	349.2	99.6	142.4	349.4	100.2	142.9	350.2	100.2	142.2
2	349.8	99.9	142.0	350.0	100.5	142.0	349.0	100.2	142.9
3	349.6	99.6	142.4	349.4	99.9	142.4	349.1	100.2	142.6
4	349.5	99.8	142.6	349.6	100.5	142.7	349.3	100.0	142.5
5	349.8	100.3	142.8	349.8	100.3	142.9	349.8	100.3	142.8
6	349.7	99.7	142.0	349.0	99.5	142.0	349.2	100.2	142.7
7	349.8	100.1	142.1	349.1	99.8	142.7	349.6	100.1	142.8
8	349.4	99.4	142.3	349.3	99.5	142.3	349.9	99.9	142.4
9	349.1	100.7	142.2	349.2	99.7	142.7	349.7	99.6	142.1
10	349.4	100.0	142.6	349.6	100.1	142.6	350.0	99.8	142.4
11	349.1	99.6	142.4	349.4	99.9	142.4	349.6	99.6	142.1
12	349.5	100.4	142.7	349.7	100.6	142.7	349.9	100.0	142,5
13	349.3	100.1	142.5	349.5	100.0	142.5	349.6	99.8	142.3
14	349.5	100.4	142.8	349.8	100.3	142.9	349.9	100.0	142.5
15	349.4	100.6	142.9	349.9	100.4	142.1	350.1	99.7	142.4
16	349.5	99.6	142.0	349.0	100.0	142.9	349.1	100.2	142.5
17	349.6	100.4	142.7	349.7	99.9	142.7	349.9	100.4	142.6
18	349.6	100.2	142.6	349.6	100.4	142.6	349.7	100.1	142.5
19	349.4	100.6	142.8	349.8	100.0	142.8	350.1	99.9	142.4
20	349.7	100.1	142.6	349.6	100.3	142.6	350.0	99.7	142.7

Table 3

Metrological characteristics SEG-002 "AKP-P"

Metrological characteristic	Value
Extended uncertainty of registration effectiveness ($k = 2$, $P = 0.95$), %	6.0
Range of gamma radiation energies, keV	from 50 to 2800
The energy resolution along the line is 1332 keV, keV	2.0
Integral nonlinearity, %	0.03
Long-term instability for calibration characteristic for 8 hours of operation, %	0.06

Table 4

Study of homogeneity between samples Th-232

Discrepancy source	Square sums (SS)	Degrees of freedom (DF)	Mean square (MS)
Between samples	1.46	19.0	0.0766
Within samples	2.77	40.0	0.0691
Total disagreement	4.23	59.0	–

To measure the specific activity, the following conditions shall be observed: 19 °C of ambient temperature; 31% of relative humidity; 98.3 kPa of atmospheric pressure.

During further calculations, dispersion analysis (ANOVA – Analysis of Variation) was applied. This analysis is convenient to process data and evaluate the components of measurement uncertainty that describe the homogeneity between samples or standard deviation among laboratories.

In case of the ANOVA variance analysis, the effect of the distinction between the normal activity in various groups is examined by looking at the differences across the groups. As a result of dividing the total variance into several sources, it is possible to compare the variance caused by between-group differences with the variance caused by within-group variability. When testing the hypothesis, the fact that there is no difference between the groups is established. If the null hypothesis is true, the estimate of the variance associated with within-group variability should be close to the estimate of the group variance. If it is false, the values significantly differ by a wide margin [5, 6].

Table 4 shows the variance analysis which can be obtained on an Excel spreadsheet and with the ANOVA package for Th-232 (as example).

In this way, taking into account the guidelines of DSTU-N ISO Guide 35:2018, the change (variance) in the values measured for certain behaviour of the samples of Th-232 can be obtained as follows:

$$S^2_{between} = \frac{MS_{between} - MS_{within}}{n_0} = \frac{0.0766 - 0.0691}{3} = 0.0025 \ \left(\text{Bq} \cdot \text{kg}^{-1}\right).$$

The square root of the variance is the standard deviation across the samples, which is:

$$S_{bb} = \sqrt{0.0025} = 0.05 \ \text{Bq} \cdot \text{kg}^{-1}.$$

The repeatability standard deviation can be obtained as:

$$S_r = \sqrt{MS_{within}} = \sqrt{0.0691} = 0.2628 \ \text{Bq} \cdot \text{kg}^{-1}.$$

The calculation results for Eu-152, Cs-137, and Th-232 are provided in Table 5.

The repeatability standard deviation is covered by the uncertainty of the results of SEG-002 "AKP-P" measurements.

Assessment of material stability

An important condition for the intended use of a reference material is the sufficient stability of its characteristics, so that the assigned value is anytime reliable for users as long as the certificate on the reference material is valid. Typically, the stability under conditions of long-term storage, during transportation, and, if possible, under the conditions of storage at the user's laboratory shall be considered.

Table 5

The results for Eu-152, Cs-137, and Th-232

$S^2_{between}$	S_{bb}	S_r
Eu-152		
0.00442	0.07	0.2975
Cs-137		
0.96	0.98	1.36
Th-232		
0.0025	0.05	0.2628

Table 6

The measurement results during the investigation of the stability of Eu-152 material

Time (days)	Calc. activity taking into account the half-life, Bq	The measured activity of the material, Bq	Diff. Δ_{2-1}, Bq	Expanded uncertainty of measurement results, U, Bq	$\lvert\Delta_{2-1}\rvert$ / U, Bq
0	6990.00	6990.00	0	0	0
30	6959.46	6958.48	-0.98	418	0.0024
60	6929.04	6930.06	1.02	416	0.0025
90	6898.76	6899.75	0.99	414	0.0024
120	6868.61	6870.58	1.97	412	0.0048
150	6838.60	6837.62	-0.98	410	0.0024
180	6808.72	6807.74	-0.98	408	-0.00240
210	6778.96	6779.93	0.97	407	0.00238
240	6749.34	6751.27	1.93	405	0.00476
270	6719.85	6721.77	1.92	403	0.00476
300	6690.48	6689.53	-0.95	401	-0.00237
330	6661.25	6656.95	-4.30	399	0.0108
360	6632.14	6631.19	-0.95	398	0.0024

Table 7

The results of the stability study of Cs-137 material

Time (days)	The measured activity of the material, Bq/kg
0	2015.1
30	2012.2
60	1999.6
90	1998.9

As part of the conducted work, the material (a special-purpose radionuclide source) underwent stability research regarding the reproduction of Eu-152 content. The experimental data obtained during the initial, 30, 60, 90, 120, 150, 330, and 360 days are presented in Table 6. In Table 6, the measurement results are compared with the calculated activity obtained taking into account the half-life period of Eu-152.

The measurement results of the material (radioactive source of special designation – OISN-1) underwent an investigation into the stability of Cs-137 content reproduction. The experimental data are presented in Table 7. Since the work is limited to three months (April – June 2021), the stability study was conducted for a period of 90 days.

According to [7], the difference Δ_{2-1} is compared to the uncertainty of the measurement result. If the difference exists and $\lvert\Delta_{2-1}\rvert/U>1$, it means that the difference Δ_{2-1} cannot be explained by the uncertainty alone but can be attributed to any changes in the reference material during the investigation period. If $\lvert\Delta_{2-1}\rvert/U<1$, it can be concluded that the investigated reference material with Eu-152 content is stable. The same with Cs-137 [8] and Th-232.

The obtained experimental data during the initial, 30, 60, 90, 120, 150, 330, and 360 days equaled 2850 Bq/kg, as Th-232 is the most long-lived isotope with a half-life of 1.405×10^{10} years, which is three times longer than the age of the Earth and comparable to the age of the Universe.

Evaluation of the measurement uncertainty of reference materials

The activity is measured by the gamma-spectrometric method to determine the composition of nuclides, and the Marinelli beakers of the capacity that suits best.

Table 8

The budget of measurement uncertainty for Eu-152

Standard measurement uncertainty, rel. units	A	B
Rate of counting	0.010	–
Efficiency	–	0.023
Mass	0.0002	–
Coefficient of quantum yield	–	0.00225
Combined standard measurement uncertainty	0.025	
Expanded measurement uncertainty, $k = 2$, $p = 0.95$, %	5.0	

Table 9

The budget of measurement uncertainty for Cs-137

Standard uncertainty, rel. units	A	B
Rate of counting	0.009	–
Efficiency	–	0.034
Mass	0.0002	–
Coefficient of quantum yield	–	0.0024
Combined standard measurement uncertainty	0.035	
Expanded measurement uncertainty, $k = 2$, $p = 0.95$, %	7.0	

Table 10

The budget of measurement uncertainty for Th-232

Standard uncertainty, rel. units	A	B
Rate of counting	0.010	–
Efficiency	–	0.023
Mass	0.0002	–
Coefficient of quantum yield	–	0.00235
Combined standard measurement uncertainty	0.025	
Expanded measurement uncertainty, $k = 2$, $p = 0.95$, %	5.0	

The budget of the measurement uncertainty [9] for reference materials that contain Eu-152, Cs-137 and Th-232 is given in Table 8–10.

So, for the specific activity set value of the materials under consideration, the expanded measurement uncertainty is covered by the range 5.0–7.0%, respectively.

Discussion of the results

The homogeneity properties and stability of the OISN-1 and KOISN sources, fragments with Eu-152, Cs-137 and Th-232, using the quartering technique according to existing international regulations have been established and considered.

The grounds for additional studies of metrological characteristics of the reference materials that are used in the legal metrology field have been substantiated.

The homogeneity properties and stability of maintaining and reproducing the measurement unit of activity, Bq, are provided by the reference materials of Eu-152, Cs-137 and Th-232 that are produced by the manufacturer. With the applied assessment method, according to [1] and other international regulations, metrological traceability of the reference materials to the national measurement standards of Ukraine in ionizing radiation is ensured. The preliminary data for further studies have been amassed.

Taking into account Ukraine's accession to the Metric Convention and active participation in the CIPM MRA Agreement, there is a need to intensify efforts for further use of international normative documents in the performance of scientific metrological work.

Considering the existing problem of environmental contamination with technogenic radionuclides (industrial emissions, active and closed power units of nuclear power plants in Ukraine), it is necessary to continue work on metrological control of sources of ionizing radiation.

Conclusions

From scientific and practical point of view, the significance of the work and obtained results is that the values obtained for the stability and homogeneity of the reference standard materials (Eu-152 OISN №01-095-10, Cs-137 OISN №01-140-14, Th-232 KOISN №01-0014-04), which are the source of reference materials of Eu-152, Cs-137 and Th-232, may be used in research to find the values of the activity of the generated reference samples as the amount of elementary radioactive decays in one gram of Eu-152, Cs-137 and Th-232 including the values of measurement uncertainties, considering the guidelines of DSTU-N ISO Guide 35:2018.

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Статистичний метод оцінки метрологічних характеристик стандартних зразків

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Анотація

Об'єктом досліджень є стандартні зразки: європій-152, цезій-137, торій-232, які передбачається застосовувати у сфері законодавчо регульованої метрології під час проведення повірки законодавчо регульованих засобів вимірювальної техніки.

Стандартні зразки складу та властивостей речовин і матеріалів застосовують у виробничій та невиробничій сферах діяльності суспільства для забезпечення єдності вимірювань та простежуваності в тих видах вимірювань, які не можуть бути забезпечені за допомогою еталонів.

У період війни та посилення ядерної загрози внаслідок повномасштабного вторгнення агресора необхідно приділяти підвищену увагу перевірці блоків виявлення іонізуючого випромінювання, вимірювальних каналів систем радіаційного контролю, радіометрів, радіометричних установок, а також спектрометрів альфа-, бета- та гамма-випромінювання.

Однорідність є основною вимогою для всіх стандартних зразків і включає до себе як однорідність у межах екземпляра, так і однорідність між екземплярами, яка є важливою для однакових значень внутрішньо-екземплярної однорідності.

Метою статті є демонстрація методу оцінки невизначеності вимірювань еталонних матеріалів, коли вони генеруються та калібруються, відповідно до міжнародних правил. Оцінка похибки вимірювання радіоактивного еталонного матеріалу з природним періодом напіврозпаду є актуальною та дійсною, враховуючи його властивості однорідності та стабільність. Для оцінки властивостей, а також похибки вимірювання було проведено одноваріантний дисперсійний аналіз.

Наукова та практична цінність результатів виконаних робіт полягає в тому, що отримані значення однорідності та стабільності матеріалів, із яких створюються стандартні зразки, а також встановлені значення активностей цих зразків, відповідають вимогам міжнародних нормативних документів.

Ключові слова: радіаційний контроль; еталонні матеріали; властивості однорідності; стабільність; невизначеність вимірювань; метрологічні характеристики.

References

1. ISO GUIDE 35:2017. Reference materials – Guidance for characterization and assessment of homogeneity and stability. 105 p.
2. ILAC G12:2000. Guidelines for the Requirements for the Competence of Reference Materials Producers. 30 p.
3. Lamberty A., Schimmel H., Pauwels J. The study of the stability of reference materials by isochronous measurements. *Fresenius Journal of Analytical Chemistry*, 1998, vol. 360(3), pp. 359–361. doi: 10.1007/s002160050711
4. DSP 6.177-2005-09-02. Basic sanitary rules for ensuring radiation safety of Ukraine. Kyiv, 2005 (in Ukrainian).
5. Scheffe H. The Analysis of Variance. New York, John Wiley and Sons, 1959. 496 p.
6. Lapach S.N., Chubenko A.V., Babich P.N. Statistika v nauke i biznese [Statistics in science and business]. Kiev, Morion, 2002. 640 p.
7. Ellison S.L.R. and Williams A. (Eds). Eurachem/CITAC Guide: Metrological Traceability in Analytical measurement. 2nd ed. 2019. ISBN: 978-0-948926-34-1. Available at: www.eurachem.org
8. Skliarov V., Degtiarov O., Zaporozhets O., Letuchy O., Ievsieiev V. Utilizing of Univariate Analysis of Variance for Evaluation of Uncertainties Measurement Results of Properties of Reference Materials. *Proceedings of XXXII International Scientific Symposium Metrology and Metrology Assurance (MMA)*, Sozopol, Bulgaria, 2022. doi: 10.1109/MMA55579.2022.9992863
9. Zakharov I.P., Vodotyka S.V., Klimova K.A., Shevchenko N.S. Some examples of the evaluation of measurement uncertainty. *Measurement Techniques*, 2013, vol. 56(6), pp. 591–598. doi: 10.1007/s11018-013-0250-x