РОЗДІЛ 2. Благополуччя довкілля та екологічна безпека
SECTION 2. Environmental well-being and safety

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ASSESSMENT OF THE SUITABILITY OF THE SPECTROMETRIC METHOD OF MEASURING THE SPECIFIC ACTIVITY OF CESIUM-137 IN WATER SAMPLES USING SCINTILLATION GAMMA SPECTROMETER AND SOFTWARE "PROGRESS"

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Abstract. *Cesium-137 is one of the primary radionuclides used as an indicator of environmental radiological contamination. Due to its relatively long half-life (30 years), it poses a significant radiological hazard, as it can penetrate and accumulate in various tissues and organs, causing internal exposure.*
To prevent the accumulation of radionuclides in the human body and reduce associated health risks, as well as to ensure the safety of food products in Ukraine and the European Union, maximum permissible levels of cesium-137 in food are regulated at the legislative level. Radiological monitoring of foodstuffs is routinely conducted using gamma-spectrometric analysis, which allows for rapid identification and quantification of radionuclide content.
According to DSTU EN ISO/IEC 17025:2019 General Requirements for the Competence of Testing and Calibration Laboratories, all analytical methods used by state laboratories must be validated and accredited.
This article describes the procedure for conducting abbreviated validation of the method for measuring the specific activity of cesium-137 in control water samples artificially enriched with the analyte, using a scintillation gamma spectrometer. The study was conducted at the State Research Institute for Laboratory Diagnosis and Veterinary and Sanitary Expertise. The suitability of the method for its intended purpose was evaluated based on key parameters such as measurement accuracy and intermediate precision.
The validation results demonstrated that the measurements of cesium-137 specific activity did not exceed the normative limits specified by the measurement method. Therefore, this method can be considered suitable for specific applications, providing accurate and reliable results.
Keywords: cesium-137, control samples, gamma spectrometry, accuracy, precision, bias, method suitability

Radioactive contamination of the environment is considered one of the greatest dangers of the modern world, as radioactivity can negatively affect both the environment and its inhabitants for many years (Gupta, 2018; IAEA, 2011; Kashparov, 2019; Russell, 2015).

According to literature data, the radionuclides cesium-137 and strontium-90 play the most significant role in the radiological contamination of the biosphere. Due to their relatively long half-lives—30 years for cesium-137 and 29 years for strontium-90—they can accumulate significant doses of radiation (Jeskovsky, 2019; Kotelevych, 2019; Malimon, 2023). The main sources of these radionuclides entering the air environment are nuclear tests and accidents at nuclear power plants (Fesenko, 2013; IAEA, 2019).

One of the main radionuclide contaminants in food consumed by humans is cesium-137 (Zdrojewicz, 2016; Romanchuk, 2019). Long-term consumption of products contaminated with radiocesium can cause inflammatory processes in various tissues and organs of the human body, with the most pronounced inflammation observed in the gastrointestinal tract, urinary tract, and reproductive system (Dutov, 2015; Gudkov, 2012; Godyn, 2016; Konoplev, 2020). To prevent the accumulation of radionuclides in the human body and reduce the negative impact of radiation on health, as well as to ensure the population has safe food, Ukraine and the European Union have legally established maximum permissible levels of cesium-137 in

food products. Additionally, in accordance with current regulations, systematic monitoring of food products for radiological indicators, including the measurement of cesium-137 and strontium-90 content using spectrometric analysis methods, is conducted. These methods allow for rapid identification and quantitative determination of radionuclide content in the matrix (Zdrojewicz, 2016).

According to DSTU EN ISO/IEC 17025:2019 General requirements for the competence of testing and calibration laboratories, all methods used by state laboratories of the State Consumer Service of Ukraine must be validated and accredited. Validation provides an understanding of the capabilities and limitations of the method during routine use and ensures the reliability of the obtained results (Initial validation and transfer, 2010; Eurachem guide, 2016; ISO17025:2019; ISO 5725).

The aim of study. To determine the suitability of the spectrometric method for measuring the specific activity of cesium-137 in water samples using a scintillation gamma spectrometer and Progress software.

Materials and methods. The research was conducted at the State Scientific and Research Institute for Laboratory Diagnostics and Veterinary and Sanitary Expertise, Kyiv, Ukraine. The test material consisted of control water samples enriched at a level of 1.80 Bq/kg with a standard solution of cesium-137 radionuclide type RR^{137}Cs No. 08-030-24, with a nominal volumetric activity of cesium-137 of 100 Bq/kg ±20%.

Measurements of the specific activity of cesium-137 in the control samples were performed using the Gamma Plus universal spectrometric complex with an NaI detection block and Progress software.

Results and discussion. This article describes the parameters used for the abbreviated validation of the scintillation gamma spectrometry method using control samples enriched with cesium-137 analyte. The research included the specifics of the measurement method, taking into account all critical stages of the process. The suitability of the method for the intended purpose was confirmed based on key parameters such as the accuracy and intermediate precision of the measurement results (Initial validation and transfer, 2010; ISO17025:2019; ISO 5725).

Before starting the measurements, preliminary preparation of the control samples was performed using the physical concentration method. The specific activity of cesium-137 was measured according to the methodology for measuring radionuclide activity using a scintillation gamma spectrometer with software "Progress".

The accuracy of the measurements was assessed under conditions of intermediate convergence. For this purpose, one operator conducted ten consecutive studies of the control samples using the same measurement method, the same instrument, while changing one factor (day of measurement).

The obtained measurement results were processed using generally accepted statistical methods and are presented in Table 1.

The accuracy of the measurement expresses how close the average value of an infinite number of measurement results is to the reference value. Since it is impossible to perform an infinite number of measurements, the accuracy was evaluated through «bias». For this purpose, the average value of the ten measurements, which was 1.89 Bq/kg, was compared with the reference value of 1.80 Bq/kg. According to the obtained data, the "bias" value can be considered insignificant, as it was only 0.09 Bq/kg.

Figure 1 shows a histogram evaluating the accuracy of the measurements by determining the percentage recovery of the added analyte (cesium-137) to the matrix (water).

Table 1

Results of measurements of control samples enriched with cesium-137

Research days	Added standard at the level, Bq/kg	Parameters of the state of the premises			Measurement results, Bq/kg	Standard deviation, (S), Bq/kg	Relative standard deviation (RSD), %	Bias (b), Bq/kg
		Temperature, °C	Humidity, %	Atmospheric pressure, kPa				
1	1.80	20	58	100.0	1.71	0.12	6.50	0.09
2		20	63	100.3	1.96			
3		20	63	100.3	1.97			
4		20	67	100.6	1.98			
5		20	63	100.1	1.83			
6		20	67	100.3	1.98			
7		20	64	100.8	2.05			
8		20	55	100.3	1.68			
9		20	58	100.0	1.90			
10		20	63	100.3	1.84			

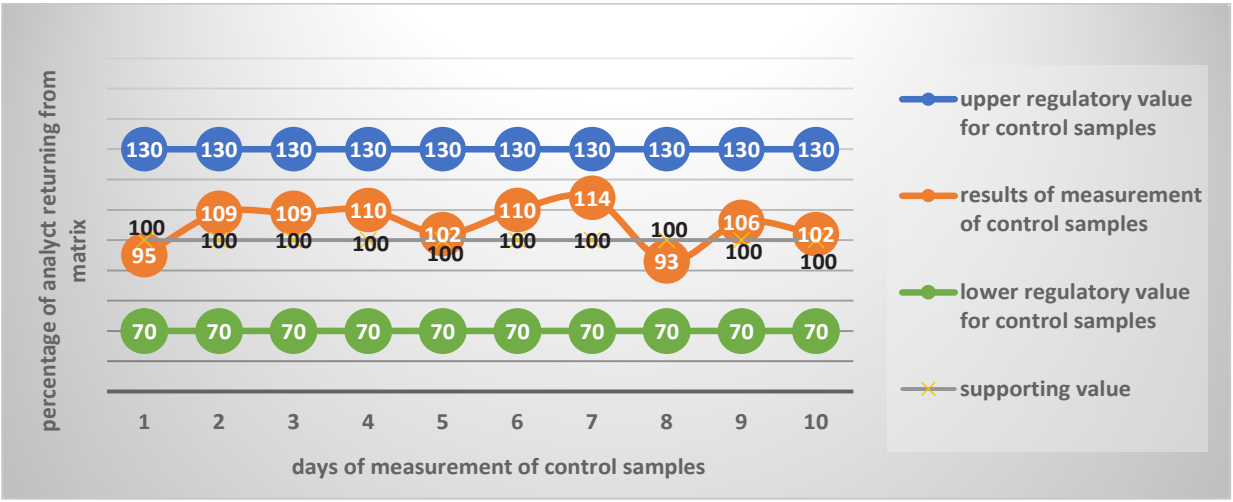

Fig.1. Percentage recovery of the added cesium-137 analyte in the control water samples

Analyzing the histogram data, it is noted that the percentage recovery of the analyte in the measured control samples enriched with cesium-137 relative to the reference value of 1.80 Bq/kg (100%) ranged from 93% to 114%. Therefore, the measurement results can be considered acceptable and reliable, as they fall within the normative value (100±30%) specified by this measurement method.

The second important indicator for evaluating the suitability of the method is the intermediate precision of the measurements, usually expressed by statistical parameters characterizing the dispersion of measurement results, such as convergence and intra-laboratory reproducibility.

In this work, we used the method of simultaneously determining convergence and intra-laboratory reproducibility of measurement results described in ISO 5725-3:2005 Accuracy (trueness and precision) of measurement methods and results. For this purpose, three series of measurements were conducted, with three measurements in each series. Convergence was assessed within one series (measurements were performed by one operator on the same instrument within one day). Intra-laboratory reproducibility of the measurement results of the control samples was performed under maximally different conditions (series), with tests

conducted by different operators on different instruments on different days. The results of the measurements are presented below in Table 2.

Table 2

Results of measurements of the specific activity of cesium-137 in control samples under conditions of convergence and intra-laboratory reproducibility

Research days	Parameters of the state of the premises			Measuring series	Measurement results, Bq/kg		
	Temperature, ºC	Humidity %	Atmospheric pressure, kPa		X_1	X_2	X_3
1	20	63	100.2	A	1.87	1.67	1.62
2	21	55	100.0	B	1.79	1.96	1.83
3	21	59	99.6	C	1.86	2.13	1.82
Relative standard deviation of convergence, %						7.07	
Relative standard deviation of convergence of internally laboratory reproduction, %						8.16	

According to the data in the table, the smallest spread of measurement results was observed when conducting studies under convergence conditions. In contrast, conducting studies under intra-laboratory reproducibility conditions was accompanied by an increase in the variability of measurement results and a greater spread between them.

Since precision depends on the concentration of the analyte in the control sample, it is advisable to express it through the relative standard deviation. The calculation of the relative standard deviation was performed in accordance with the Guideline Fitness for Purpose of Analytical Methods. A Laboratory Guide to Method Validation and Related Topics (Eurachem guide, 2016). The relative standard deviation of convergence was evaluated as intra-group precision and amounted to 7.07%, while the relative standard deviation of intra-laboratory reproducibility—as the square root of the sum of the squares of intra-group and inter-group precision—was 8.16%.

In summary, the obtained data indicate that this method is suitable for use, as the obtained values of the relative standard deviation of convergence and the relative standard deviation of intra-laboratory reproducibility did not exceed the relative standard deviation established by the measurement method (no more than 30%).

Conclusions.

Based on the obtained and analyzed results of the abbreviated validation of the methodology for determining the specific activity of cesium-137 using a scintillation gamma spectrometer and the Progress software, the method was found to meet key validation criteria. In particular, the accuracy of the measurements evaluated by bias and the percentage recovery of the analyte added to the matrix as well as the precision of the measurements, including convergence and intra-laboratory reproducibility, were assessed using control water samples.

The validation data confirmed that under highly variable measurement conditions, the method provides accurate and statistically reliable results. Therefore, the analytical method can be considered suitable for further application in the radiological monitoring of food products and water.

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ОЦІНКА ПРИДАТНОСТІ СПЕКТРОМЕТРИЧНОГО МЕТОДУ ВИМІРЮВАННЯ ПИТОМОЇ АКТИВНОСТІ ЦЕЗІЮ-137 В ЗРАЗКАХ ВОДИ З ВИКОРИСТАННЯМ ГАММА-СПЕКТРОМЕТРА ТА ПРОГРАМНОГО ЗАБЕЗПЕЧЕННЯ «ПРОГРЕС»

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Резюме. *Цезій-137 є одним із головних радіонуклідів, який служить індикатором радіологічного забруднення навколишнього середовища. Завдяки своєму відносно довгому періоду напіврозпаду (30 років) радіоцезій вважається найбільш небезпечним джерелом гамма опромінення, оскільки здатний проникати та накопичуватися у різних тканинах та органах організму, спричиняючи його внутрішнє опромінення.*

З метою запобігання накопичуванню радіонуклідів в організмі людини та зменшення впливу негативних факторів на її здоров'я, а також з метою забезпечення населення безпечними харчовими продуктами в Україні та в країнах Європейського Союзу на законодавчому рівні регламентуються максимально допустимі рівні цезію-137 в харчових продуктах. Також на постійній основі проводиться моніторинг харчових продуктів за радіологічними показниками методом гамма-спектрометричного аналізу, який дозволяє швидко ідентифікувати та кількісно визначати вміст радіонуклідів.

Виходячи з того, що відповідно до ДСТУ EN ISO/IEC 17025:2019 «Загальні вимоги до компетентності випробувальних та калібрувальних лабораторій» усі методи якими володіють державні лабораторії для визначення показників безпеки та якості харчових продуктів повинні бути валідованими (верифікованими) та акредитованими.

У даній статті описано процедуру проведення верифікації методики вимірювання питомої активності цезію-137 в контрольних зразках води штучно збагачених аналітом цезію-137 з використанням сцинтиляційного гамма-спектрометра. Дослідження проводилися на базі Науково-дослідного інституту з лабораторної діагностики та ветеринарно-санітарної експертизи. Підтвердження придатності даного методу поставленим цілям оцінювали за такими ключовими параметрами, як: правильність та проміжна прецизійність результатів вимірювань.

Оскільки, по усім аналізуючим параметрам, результати вимірювань питомої активності цезію-137 не перевищували нормативні значення зазначенні методикою вимірювань, можемо стверджувати що даний метод придатний для конкретного застосування, а отримані результати вимірювань є правильними та достовірними.

Ключові слова: цезій-137, контрольні зразки, гамма-спектрометрія, правильність, прецизійність, «зсув», придатність методу

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