

Calibration of the Alpha-Spectrometry System for Radiological Evaluation of Systems and Equipment Subject to Decommissioning at Units 1-4 of Kozloduy NPP

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Abstract. During the radiological inventory evaluation of systems and equipment subject to decommissioning at units 1-4 of Kozloduy NPP, and for the purpose of radioactive waste characterization, it is necessary to determine the activity of a number of difficult-to-measure alpha-emitting radio nuclides (isotopes of uranium, plutonium, americium and curium). Their determination requires destructive analysis involving radiochemical separation of alpha-nuclides and alpha-spectrometric measurement of sources prepared via electrodeposition.

This work discusses approaches to develop and validate a calibration method of the alpha-spectrometry system used for determination of the activity of alpha-emitting radio nuclides (²⁴¹Am, ^{238,239/240}Pu, ^{234,235,238}U).

Keywords: alpha-spectrometry, calibration, uncertainty, decommissioning.

1 Introduction

The assessment of the radiological status of the equipment and premises during the decommissioning of a nuclear installation (radiological characterization of facilities) is one of the main tasks of the process of “Decommissioning”. In order to characterize radioactive waste, it is necessary to determine the activities of several difficult-to-measure (DTM) radio nuclides, some of which are alpha-emitters (isotopes of uranium, plutonium, americium and curium). To determine the activity of alpha radio nuclides in different samples destructive analysis is needed including radiochemical separation and measurement of the prepared samples using a calibrated alpha-spectrometry system. To ensure the identification and quantification of the activity of alpha-nuclides efficiency calibration of the alpha-spectrometry system should be performed and the dependence between the energy of the alpha-particles and the channel number should be established.

2 Calibration of Alpha-Spectrometry System

The purpose of calibration is to establish the relationship between the number of registered signals (counts) per minute and the number of radioactive decays per minute of the radionuclide, which is determined. The calibration of the alpha-spectrometry system is performed with a source that is as similar as possible to the samples to be measured obtained by radiochemical processing. The calibration of the alpha-spectrometry system in Section Radiochemistry was performed using a certified reference material (CRM) prepared of Analytix (USA) by electrodeposition of mixture of radio nuclides on a stainless steel disk. The calibration procedure involves measurement of the CRM and determination of the counting efficiency in the specified

measurement geometry. For the purpose of validation of the calibration method three measurements of the CRM were performed using one of the detectors of the system at a certain detector-source distance. Upon completion of the individual measurements, each of them was used to perform calibration using the system’s software [1] and using independent manual calculations. Two of the measurements were carried out under repeatability conditions and the one under reproducibility conditions with respect to the other two.

The long measurement time of the CRM and the performance of calibration by a single measurement define that a small number of measurements are sufficient for validation. The source used in this work contains four isotopes – ²³⁰Th, ²³⁹Pu, ²⁴¹Am and ²⁴⁴Cm and is traceable to the National Institute of Science and Technology (NIST). The diameter of the active spot of the source is 24 mm. The alpha-counting efficiency in the presence of several radio nuclides in the CRM is determined according to the expression:

$$E_{ff} = \frac{1}{n} \sum_i^n \left(\frac{cpm_i}{dpm_i D_i R_i} \right), \quad (1)$$

where E_{ff} is the counting efficiency; n is the number of the nuclides in the CRM; cpm_i is the counting rate in the region of interest (ROI); dpm_i is the activity given by the manufacturer’s certificate, expressed as the number of decays per minute; D_i is the decay correction factor; R_i is the yield of alpha-particles (α – yield) in the specified ROI.

The expanded uncertainty of the efficiency is given as

$$U(E_{ff}) = k u(E_{ff}). \quad (2)$$

Here the combined uncertainty $u(E_{ff})$ is multiplied by a coverage factor of $k = 2$, which for a normal

distribution corresponds to a confidence level of approximately 95% [2].

The combined uncertainty of the counting efficiency is

$$u(E_{ff}) = \frac{1}{n} \sqrt{\sum_i^n u^2(E_{ff_i})}, \quad (3)$$

where $u(E_{ff})$ is the combined uncertainty of the counting efficiency in the given measurement geometry; $u(E_{ff_i})$ is the combined uncertainty of the counting efficiency of a single nuclide present in the CRM.

The relative combined uncertainty of the counting efficiency for a single nuclide is calculated as

$$w(E_{ff_i}) = \sqrt{w_{cpm_i}^2 + w_{dpm_i}^2 + w_{D_i}^2 + w_{R_i}^2}, \quad (4)$$

where w_{cpm_i} is the relative uncertainty of the counting rate; w_{dpm_i} is the relative uncertainty of the activity as stated in the certificate; w_{D_i} is the relative uncertainty of the correction for radioactive decay; w_{R_i} is the relative uncertainty of the α - yield.

Table 1 shows the uncertainty budget of the counting efficiency determined by the calibration procedure.

To assess the uncertainty in the efficiency calibration procedure Spreadsheet approach was also used [3,4]. The theoretical bases of the application of Spreadsheet approach are presented in [5]. This approach is relatively quick and easy method to evaluate the combined uncertainty, having already estimated the uncertainties of the individual components.

Below the values obtained for the registration efficiency and its expanded uncertainty estimated in three ways (assessed by the specialized software, by manual calculations

and by the Spreadsheet approach) for one of the measurements are given.

ORTEC Software	E_{ff} (21.93 ± 0.45)%
Manual Calculation	E_{ff} (21.93 ± 0.50)%
Spreadsheet	E_{ff} (21.93 ± 0.49)%

As can be seen, there is a very good correspondence between the results for the registration efficiency and quite small difference between the estimates of the uncertainty. The obtained results verify the usage of the software of the alpha-spectrometry system for calibration.

For validation of the method for calibration of the alpha-spectrometry system, the characteristics repeatability and reproducibility, and the uncertainty were investigated.

For validation of the repeatability and reproducibility of the registration efficiency E_n -criterion is used

$$E_n = \left| \frac{E_{ff1} - E_{ff2}}{\sqrt{U_{E_{ff1}}^2 + U_{E_{ff2}}^2}} \right| \leq 1, \quad (5)$$

where E_{ff} is the alpha-counting efficiency; $U_{E_{ff}}$ is the expanded uncertainty of the counting efficiency [6]; and the indexes 1 and 2 correspond to the different measurements.

This criterion requires that the absolute difference in the efficiency values does not exceed the expanded uncertainty of this difference. If the criterion is fulfilled, the two results are virtually indistinguishable within their uncertainties.

Table 1. Uncertainty budget

Source of uncertainty	Symbol	Value	Uncertainty	Probability distribution	Relative uncertainty	Type of uncertainty
Activity by certificate	$dpm_{s, Th-230}$	100 dpm	2 dpm	normal	2.00%	B, Combine
Counting rate	cpm_{Th-230}	22.236 cpm	0.149 cpm	normal	0.67%	B
Alpha-yield	R_{Th-230}	0.9982	0.0058	rectangular	0.58%	B
Decay correction factor	D_{Th-230}	0.999975	2.49E-8	exponential	2.49E-6%	B, Combine
Counting efficiency	$E_{ff Th-230}$	0.2228			2.19%	B, Combine
Activity by certificate	$dpm_{s, Pu-239}$	116 dpm	2.5 dpm	normal	2.16%	B, Combine
Counting rate	cpm_{Pu-239}	25.117 cpm	0.158 cpm	normal	0.63%	B
Alpha-yield	R_{Pu-239}	1.0001	0.0058	rectangular	0.58%	B
Decay correction factor	D_{Pu-239}	0.999921	7.94E-8	exponential	7.94E-6%	B, Combine
Counting efficiency	$E_{ff Pu-239}$	0.2165			2.32%	B, Combine
Activity by certificate	$dpm_{s, Am-241}$	108 dpm	2.5 dpm	normal	2.31%	B, Combine
Counting rate	cpm_{Am-241}	23.676 cpm	0.154 cpm	normal	0.65%	B
Alpha-yield	R_{Am-241}	0.9997	0.0058	rectangular	0.58%	B
Decay correction factor	D_{Am-241}	0.995585	4.37E-6	exponential	4.39E-4%	B, Combine
Counting efficiency	$E_{ff Am-241}$	0.2203			2.47%	B, Combine
Activity by certificate	$dpm_{s, Cm-244}$	105 dpm	2.0 dpm	normal	1.90%	B, Combine
Counting rate	cpm_{Cm-244}	20.564 cpm	0.143 cpm	normal	0.70%	B
Alpha-yield	R_{Cm-244}	1.0000	0.0058	rectangular	0.58%	B
Decay correction factor	D_{Cm-244}	0.899528	1.05E-4	exponential	1.17E-2%	B, Combine
Counting efficiency	$E_{ff Cm-244}$	0.2177			2.11%	B, Combine
$E_{ff Det 2-8 mm}$		0.2193			1.14%	B, Combine

Repeatability – characterizes the correspondence between the results of successive measurements of the same variable parameter performed under the same conditions – using the same method of measurement, by the same operator, with the same measurement equipment and CRM, and in the shortest possible interval between measurements [7].

Results of the efficiency calibration
(under repeatability conditions)

$$E_{ff2} (21.97 \pm 0.45)\%$$

$$E_{ff3} (21.98 \pm 0.45)\%$$

$$E_n = 0.0157$$

Reproducibility assesses the degree of similarity between the results of measurements of the same variable/parameter performed with a change in some conditions [7].

The measurements performed under different conditions are number 1 and 3 – they were performed by a different employee after a long period of time (21 days).

Results of the efficiency calibration
(under reproducibility conditions)

$$E_{ff1} (21.93 \pm 0.45)\%$$

$$E_{ff3} (21.98 \pm 0.45)\%$$

$$E_n = 0.0786$$

For validation of the reproducibility a source was prepared by direct dropping of a standard solutions of the isotopes ^{242}Pu and ^{243}Am on a stainless steel disk. The activity of this source was determined based on the mass of the applied solutions, measured by an analytical balance with 0.0001 g accuracy. The calibration procedure is repeated with the prepared source. The results are compared with the results of the calibration with the existing CRM, produced by Analytics.

Results of the efficiency calibration

CRM Analytics $E_{ff} (21.98 \pm 0.45)\%$

RM Section of Radiochemistry II $E_{ff} (22.32 \pm 1.41)\%$

$$E_n = 0.2297$$

The **uncertainty** is a parameter associated with the measurement that characterizes the dispersion of values that could be attributed to the measurand [8].

When the activity of alpha radio nuclides in a sample is determined, the result is estimated with an uncertainty, one component of which is the combined uncertainty of the counting efficiency. To reduce its contribution to the uncertainty of the outcome of the test, a requirement to the calibration method is introduced: the relative expanded uncertainty of the registration efficiency for alpha radiation should not exceed 7%. In all the cases presented here the requirement is fulfilled.

An important characteristic of the source used for calibration is the size of the active spot. The electrodeposition apparatus used in Section Radiochemistry produce active spots with diameters different from this of the CRM. Therefore, laboratory sources for calibration were prepared by electrodeposition of standard solutions of the isotopes ^{242}Pu and ^{243}Am on a stainless steel disc. Two series (5 in each series) reference materials (RM) were prepared using an electrodeposition apparatus Canberra (with diameter of the active spot of 16 mm). The two series differ in the activities of the electrodeposited radioisotopes. To verify that the radio nuclides in the solutions were fully deposited onto the stainless steel discs (after the five electrodepositions) the solutions from each series were mixed together, concentrated and electrodeposited again. Table 2 presents data for the residues of both radio nuclides in the mixed solutions as a part of the total initial activity contained in the primary solutions.

These data demonstrate that the activity of each radionuclide left over after the electrodeposition of the five sources in each series is about three orders of magnitude lower than that used for the preparation of the reference materials. The measured activity of the residue is also significantly lower than the combined uncertainty of the activity of the radionuclide for a single RM. This gives us ground to assert that practically 100% of the activity in the solution is deposited on the metal discs during the electrodeposition. Using the 10 prepared standard reference materials one of the detectors of the alpha-spectrometry system was calibrated. The results of the efficiency calibration are presented in Table 3.

Table 3. Results of the efficiency calibration

	Series 1		Series 2
Reference material	$(E_{ff} \pm U), \%$	Reference material	$(E_{ff} \pm U), \%$
cal RM 1	28.13 ± 1.30	cal RM 7	28.12 ± 0.66
cal RM 2	28.12 ± 1.30	cal RM 8	28.15 ± 0.66
cal RM 3	28.12 ± 1.31	cal RM 9	28.15 ± 0.66
cal RM 4	28.30 ± 1.31	cal RM 10	28.32 ± 0.66
cal RM 6	28.44 ± 1.32	cal RM 11	27.95 ± 0.66

Table 2. Data for the residues of both radionuclides in the solutions used for electrodeposition

Isotope	Activity, DPM					
	Series 1			Series 2		
	Total	Residue	Residue [%]	Total	Residue	Residue [%]
^{242}Pu	422.81	0.1019 ± 0.0025	0.024	846.14	0.1784 ± 0.0033	0.021
^{243}Am	425.91	0.1141 ± 0.0028	0.028	860.82	0.0460 ± 0.0020	0.005

Table 4. Results of testing CRM – NPL 2008

Isotope	Certified values NPL 2008	Values obtained in Section Radiochemistry	Deviation %
	($A \pm u$), Bq/kg	($A \pm u$), Bq/kg	
²⁴¹ Am	13.57 ± 0.04	14.82 ± 0.77	9.21
²⁴⁴ Cm	6.93 ± 0.03	6.796 ± 0.38	-1.93
²³⁸ Pu	11.86 ± 0.04	11.11 ± 0.56	-6.32
²³⁹ Pu	10.13 ± 0.05	10.15 ± 0.50	0.20
²³⁵ U	0.680 ± 0.003	0.66 ± 0.05	-2.81
²³⁴ U	14.6 ± 1.4	15.16 ± 0.592	3.84
²³⁸ U	14.76 ± 0.04	16.03 ± 0.624	8.60

The results of the calibration are acceptable since the relative expanded uncertainty of the efficiency does not exceed 7%.

The E_n -criterion is fulfilled for each combination of two results and its value is in the range of $0.0 \div 0.4$. This proves that the results of the calibration with different reference materials are indistinguishable. The activity of individual RM does not affect the counting efficiency, but only its uncertainty. The obtained results prove the applicability of each of the prepared RM for calibration.

The calibration performed by such RM was used to determine the activity of the alpha radio nuclides in samples of certified reference materials from the National Physical Laboratory, UK (NPL 2008 and NPL 2009). The test was conducted in accordance with the developed "Method for determination of isotopes of uranium, plutonium, americium and curium in water and in samples of surface-contaminated metals". The test results and their deviation from the certified values are presented in Tables 4 and 5.

The measurements of the NPL 2008 and NPL 2009 could be used to validate the test method and the method for the calibration of the alpha-spectrometry system. The deviations of the results from the certified values of the activities of all radio nuclides in the two materials do not exceed 15% and are acceptable for Section Radiochemistry.

Table 5. Results of testing CRM – NPL 2009

Isotope	Certified values NPL 2008	Values obtained in Section Radiochemistry	Deviation %
	($A \pm u$), Bq/kg	($A \pm u$), Bq/kg	
²⁴¹ Am	3.099 ± 0.006	3.447 ± 0.251	11.23
²⁴⁴ Cm	15.41 ± 0.05	14.16 ± 0.82	-8.11
²³⁹ Pu	11.68 ± 0.12	11.17 ± 0.52	-4.37
²³⁸ U	18.0 ± 0.4	17.34 ± 0.73	-3.67
²³⁷ Np	4.65 ± 0.05	4.70 ± 0.24	1.08
²³² Th	5.01 ± 0.05	5.27 ± 0.25	5.19

3 Conclusion

The method for calibration of the alpha-spectrometry system is suitable and applicable for the aims of the analysis in Section Radiochemistry.

The software for calibration developed by the supplier of the using equipment is suitable and can be used for calibration.

The testing laboratory of Section Radiochemistry can perform calibration of the alpha-spectrometry system using RM prepared in the laboratory.

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