Gamma-Ray Spectrometry Laboratory for high-precision measurements of radionuclide concentrations in environmental samples

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Abstract. The paper outlines the methodology used in the Gamma-Ray Spectrometry Laboratory for high-precision measurements of radionuclide activity concentrations in environmental samples. The Laboratory equipment includes a semiconductor detector HPGe with a 42% relative efficiency. The detector is placed in a Pb housing made of bricks 10 cm in thickness. Three measurement geometries are considered: Marinelli beakers 710 cm^3 in volume and two cylindrical geometries 121 and 48 cm^3 in volume. In the efficiency calibration ($E = 32 \div 1836$ keV) mixed gamma standard solutions were used. Obtained experimental efficiency values ε were fitted with two quadratic functions. The junction point is that equivalent to 200 keV. Uncertainty of the calibration curve is 2% for $E > 200$ keV. The relationship between the total efficiency and the energy $\varepsilon_t(E)$ was also found for energies $E = 33 \div 1250$ keV. Self-absorption correction factors C_s are calculated by the method proposed by K. Debertin, the uncertainty level being $1 \div 2\%$ for $E > 100$ keV. These correction factors are calculated by an original computer program. Coincidence summing correction factors C_c for the selected nuclides are derived using the ETNA computer program, basing on the relationships $\varepsilon(E)$ and $\varepsilon_t(E)$. Minimum detectable activity (MDA) for selected nuclides encountered in environmental samples was determined for the water matrix. The methodology used was successfully verified in the course of international intercomparison measurements.

Key words: gamma-ray spectrometry • environmental samples • efficiency • self-absorption • coincidence summing

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Introduction

Measurements of radionuclide concentrations in environmental samples have recently received a great deal of attention. The need arose to precisely measure radionuclide concentrations and the gamma-ray spectrometry method, which is of primary importance, must be improved for the purpose of these measurements. Major advancements in gamma spectrometry are now aimed at background reduction to make the nuclides better detectable and to improve the measurement accuracy, without prolonging the measurement.

The paper outlines the methodology used in the Gamma-Ray Spectrometry Laboratory of AGH-UST Faculty of Physics and Applied Computer Science, for high-precision measurements of radionuclide concentrations in environmental samples. The paper presents experimental setup, spectrometer background, measurement geometries, preparation, sealing and measurement of environmental samples, efficiency calibration, determination of concentrations of radionuclides in the samples, calculations of self-absorption and coincidence summing correction factors, detection limit determination and intercomparison measurement data. The detailed description of the methodology and the review of the literature are given elsewhere [5].

Fig. 1. Background spectrum. The spectrum is shown in the log scale to make the lines present in the background better visible. Strong background lines are identified.

Methodology

Experimental setup

The Laboratory equipment includes a semiconductor detector HPGe (Canberra GX4020) with the resolution 1.9 keV (for the line 1333 MeV), energy range above 3 keV and relative efficiency 42%. The detector is supported by an integrated spectrometric setup DeskTop InSpector (Canberra). The electronic setup is paired with a computer with an original data acquisition and the processing Genie 2000 software (Canberra), responsible for the data analysis and support of the spectrometric setup. During routine measurements, the detector is covered with hood-shaped protection cap made of polyethylene, 1.4 mm in thickness, over the detector window.

The detector is placed in a housing made of lead bricks, with a 1 mm cadmium and 1 mm copper inner lining; the upper and side walls are 10 cm in thickness, the bottom wall is 15 cm thick. The upper cover is mobile, which enables an easy replacement of samples.

Spectrometer background

The background measurements were made for an empty shield. Figure 1 shows the background spectrum, and Table 1 gives the summary, identification and count rate for selected lines present in the background. The strongest lines are chosen and those used in measurements of natural radionuclides. Presented data are the mean values of over 20 background measurements lasting from 60 to 300 h.

The background from the lines of several natural nuclides appears to vary considerably, which is caused by variations of radon concentration in the laboratory. This effect is best revealed by the strong lines of Pb-214 and Bi-214, for energy levels of several hundred keV. For example, the background count rate from the line 609.3 keV varies from 0.6×10^{-3} to 1.5×10^{-3} cps. This is revealed by a higher relative uncertainty of the average background count rate for those lines (see Table 1).

The total count rate for the energy range from 60 keV to 2650 keV is 1.9 cps or 2.1 cps·kg^{-1} per the unit of the detector mass.

Table 1. Identification and count rate for selected lines present in the spectrometer background

Energy (keV)	Nuclide	Series	Background count rate[a] (10^{-3} cps)
46.5	Pb-210	U-238	2.804(77)
72.8 + 75.0	Pb X Kα1, Kα2	Pb	9.92(19)
92.4 + 92.8	Th-234	U-238	11.79(17)
185.7 + 186.2	U-235, Ra-226	U-235, U-238	6.95(14)
238.6	Pb-212	Th-232	4.42(22)
351.9	Pb-214	U-238	1.29(21)
510.8 + 511.0	Tl-208	Th-232, annihil.	19.72(44)
583.2	Tl-208	Th-232	1.44(10)
609.3	Bi-214	U-238	1.11(16)
661.7	Cs-137		0.420(21)
1001.0	Pa-234m	U-238	0.564(52)
1460.8	K-40		3.596(45)
1764.5	Bi-214	U-238	1.043(36)
2614.5	Tl-208	Th-232	2.674(40)

[a] U_A – uncertainty in parenthesis.

Measurements

Depending on their type and accessibility, environmental samples vary in volume from several to several hundred cm^3. In order to optimize the measurement procedure, 3 geometries are used: the Marinelli beaker – a vessel of 710 cm^3 (20 mm layer of material surrounding the detector) and cylindrical geometries: 121.2 cm^3 (sample diameter 70 mm, height 31.5 mm) and 48.4 cm^3 (sample diameter 70 mm, height 12.5 mm). The samples are placed in aluminium vessels with walls 1 mm thick and positioned directly on the detector. The methodology outlined below applies to the cylindrical geometry 121.2 cm^3. As regards other geometries, the methodology is the same.

The solid material to be measured is ground below 0.5 mm, then dried to constant mass, placed in a vessel and covered with an aluminium lid. In measurements of concentration of some natural radionuclides the daughters of radon are determined, e.g. Bi-214, Ac-228, to prevent radon escape from the sample the lid-vessel connection is sealed with a gas-proof butyl compound. The sample should be sealed for about 3 weeks prior to measurements, in order to achieve the radioactivity equilibrium [7].

The duration of routine measurements is so chosen that the relative uncertainty of the counts number for the lines used in nuclide concentration calculations should be less than 5%. This time depends on the concentration of analyzed nuclides and typically ranges from 10 h to about 50 h (for Marinelli geometry from several hours to about 20 h, respectively).

Determination of nuclide concentration

The spectrometer efficiency being known, the activity of a nuclide A is derived from the formula [2]:

$$(1) \qquad A = \frac{N(E)}{T\varepsilon(E)p(E)} C_s C_c$$

where: E – the energy of photons emitted by the nuclide; $N(E)$ – the number of net counts in a photopeak corresponding to energy E; T – the measurement time; $\varepsilon(E)$ – the gamma-ray spectrometer efficiency for energy E; $p(E)$ – the gamma-ray emission probability; C_s, C_c – the correction factors to account for self-absorption in the sample and for coincidence summing, respectively.

Routine calculations of nuclide activity or activity concentration use a semi-automatic procedure supported by a report – a text file generated automatically by the Genie 2000 software during the spectrum analysis. This report contains information about the sample itself (mass, measurement geometry) and the measured spectrum (measurement time, positions and parameters of peaks, including their area). Nuclide activity concentration of a sample is computed using the dedicated computer program written in Fortran, the input includes the measurement geometry data (efficiency for selected energies, background) and the report containing the sample and spectrum data. The program feeds the required data, then computes the self-absorption correction factor C_s, nuclide concentra-
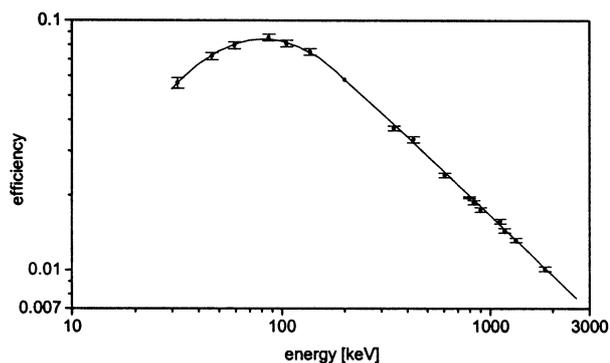
Fig. 2. Efficiency calibration curve $\varepsilon(E)$ for cylindrical geometry 121 cm^3 and for water matrix.

tions for the selected lines and their uncertainty as well as the weighted-average nuclide concentration.

The currently operated version of the program enables to determine the concentration of natural radionuclides and caesium isotopes. The program might be easily adapted to compute the concentrations of any nuclide.

Efficiency calibration

The efficiency calibration procedure uses mixed gamma standard solutions, with a 2 M HCl matrix (density 1.03 g/cm^3) or an H$_2$O matrix, containing artificial radionuclides. The uncertainty of the concentration of radionuclides present in the solutions should not exceed 2%. The 16 energy lines ranging from 32 to 1836 keV are considered (see Fig. 2). Uncertainty of the measured efficiencies would not exceed 3% (5% for $E = 32$ keV). Thus, the obtained experimental efficiency values ε are recalculated for water matrix, if necessary (correction do not exceed 1% for $E > 100$ keV). The relationship $\varepsilon(E)$ for water matrix is obtained by fitting the thus obtained values with two quadratic functions, the junction point is that equivalent to 200 keV. Uncertainty of the thus obtained calibration curve (Fig. 2) is 7% for the energy range $30 \div 50$ keV, $3 \div 4\%$ in the range $50 \div 200$ keV and 2% for energies in excess of 200 keV.

To calculate correction factor C_c, it is required that the relationship between total efficiency and energy $\varepsilon_t(E)$ should be known beforehand. In practical applications the relationship $P/T(E) = \varepsilon(E)/\varepsilon_t(E)$ (peak-to-total), is often chosen, to finally yield the total efficiency [4, 13].

In P/T measurements water solutions of nuclides emitting monoenergetic radiation (Am-241, Cs-137, Mn-54), Co-60, emitting photons of two slightly different energies, and I-131 are used. These solutions were prepared by diluting radiochemicals of unknown activity. The relationship P/T is obtained by fitting P/T values measured for the energies 33.0, 59.5, 364.5, 661.7, 834.8 and 1252.9 keV (weighted average of photon energies of Co-60). Relationship $\varepsilon(E)$ and $P/T(E)$ experimental values are further used to determine the dependence $\varepsilon_t(E)$ for the water matrix (Fig. 3). $P/T(E)$ and $\varepsilon_t(E)$ relationships in the log-log scale are nearly linear for energies in excess of about 150 keV. Thus obtained P/T and ε_t values are fitted in the log-log scale with two
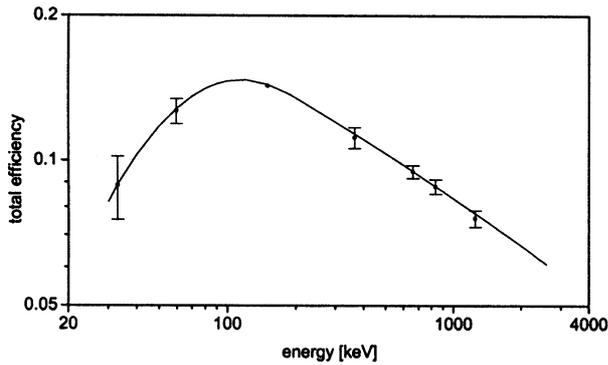
Fig. 3. Relationship $\varepsilon_t(E)$ for cylindrical geometry 121 cm³ and for water matrix.

functions: quadratic (for $E < 150$ keV) and linear (for $E > 150$ keV), the junction point is that equivalent to 150 keV. Uncertainty of the obtained calibration curve $\varepsilon_t(E)$ is 15% in the energy range $30 \div 50$ keV, 8% in the range $50 \div 150$ keV and 5% for energies in excess of 150 keV.

The relationship $P/T(E)$ for the water matrix being known, $\varepsilon_t(E)$ might be derived for other materials, too. An assumption can be made that the P/T value should be equal for all points around the given detector and independent of the material filling the space around it [8, 9]. One has to bear in mind, however, that in the case of this the uncertainty of derived value $\varepsilon_t(E)$ might be rather high.

Correction factors C_s, C_c

The formula 1 implies that in order to determine the activity of a nuclide, it is required that the correction factors C_s, C_c should be known.

The self-absorption correction factor C_s accounts for the differences in self-absorption between the sample and the standard.

The self-absorption correction factor C_s is calculated in the laboratory using the method proposed by Debertin *et al.* [2, 3]. In Debertin's method the point-like detector model is adopted and detector efficiency for the specified geometry is assumed to be proportional to the weighted sum (integral) of photons coming from individual volume elements, into which the sample may be divided. The weight of each volume element is determined by the inverse of the squared distance between this elements and point-like detector and absorption in the sample layer through which radiation can pass. The C_s factor is defined as the ratio of efficiency of standard to that of the sample, so it is equal to ratio of the mentioned above integrals calculated for standard and sample respectively. Debertin's method, widely adopted in many laboratories, gives good results, the uncertainty approaching $1 \div 2\%$ [3, 10].

A Fortran code [6] was developed in the laboratory to compute the correction factor C_s for samples in the cylindrical and Marinelli geometry, following the Debertin metod. The input data are: sample dimensions (e.g. for cylindrical samples: diameter and height) and density, distance between the point-like detector and the sample lower surface positioned over the detector and mass attenuation coefficient.
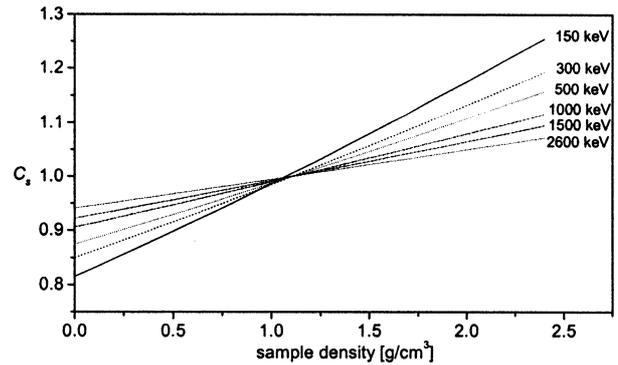
Fig. 4. $C_s(E,\rho)$ with reference to the standard for cylindrical geometry 121 cm³. It is assumed that the matrix of standard is water and that the sample displays absorption properties of silica.

In the case of precise measurements the C_s values are calculated individually for each sample, using the computer code described above.

In routine measurements of typical materials, the functional relationship $C_s(E,\rho)$ for a sample with a SiO_2 (silica) matrix is employed. The SiO_2 matrix is widely encountered in environmental samples.

In order to determine the $C_s(E,\rho)$ relationship, the C_s value was calculated for energy range $150 \div 2600$ keV and sample density range from 0.001293 g/cm³ (air) to 2.40 g/cm³, using the developed computer program. It was assumed that the matrix of standard is water and that the sample material displays the same absorption properties as silica; in other words, the mass attenuation coefficient of silica was applied. The calculated self-absorption correction does not exceed 25%. Relationship $C_s(E,\rho)$ for the SiO_2 matrix is obtained through fitting the computed C_s values with the function proposed by Bolivar *et al.* [1]:

$$(2) \quad C_s(E,\rho_s) = \exp \langle c_1 \exp[c_2(\ln E)^2)] \cdot (\rho_s - \rho_c)\rangle$$

where c_1, c_2 are adjustable parameters and ρ_s, ρ_c – density of sample and standard respectively (g/cm³).

For cylindrical geometry 121 cm³, this relationship (Fig. 4) is governed by the function:

$$(3) \quad C_s(E,\rho_s) = 0.988 *\exp \langle 0.381 \exp[-0.0301 (\ln E)^2] \cdot (\rho_s - 1.00)\rangle$$

The differences between the values of the fitting function and the C_s fitted values do not exceed 1%.

When samples of any other material are considered, then C_s values computed for silica matrix are not accurate. For example, for samples with water matrix (mass attenuation coefficient μ_m values for water and silica differ significantly), the error involved in C_s calculations is typically less than 2%.

The coincidence summing correction factor C_c must be taken into account when the measured nuclide emits photons in a cascade and when a highly efficient measurement geometry is employed, for example, for sources located near the detector (which is almost a rule in environmental measurements).

Coincidence summing correction factors C_c are typically derived from analytical formulas. The value of C_c for a volume sample is associated with nuclide nuclear data and the relationship between efficiency or total

Table 2. Coincidence summing correction factor C_c for selected nuclides for cylindrical geometry 121 cm³ and water matrix. The strongest lines of nuclides are considered, corresponding to energies in excess of 30 keV

Nuclide	Energy (keV)	C_c
Be-7	477.6	1.000
Na-24	1368.6	1.068
	2754.0	1.089
Mn-54	834.8	1.000
Co-57	122.1	1.000
	136.5	0.958
Co-60	1173.2	1.089
	1332.5	1.093
Zn-65	1115.5	1.000
Y-88	898.0	1.080
	1836.1	1.098
Cd-109	88.0	1.000
Sb-125	427.9	1.009
	635.9	1.006
I-131	284.3	1.114
	364.5	0.997
Ba-133	81.0	1.237
	356.0	1.179
Cs-134	604.7	1.133
	795.9	1.137
	1365.2	0.836
Cs-137	32.1(KX)	1.000
	661.7	1.000
Ce-139	165.9	1.073
Eu-152	344.3	1.079
	1408.0	1.197
Hg-203	279.2	1.000
Am-241	59.5	1.000

Table 3. MDA values for water matrix for the measurement time 100 h, for the cylindrical geometry 121 cm³

Nuclide	Energy (keV)	MDA (Bq/kg)
Be-7	477.6	0.75
K-40	1460.8	2.74
Co-60	1332.5	0.10
I-131	364.5	0.10
Cs-134	604.7	0.09
Cs-137	661.6	0.12
Pb-214	351.9	0.28
Bi-214	609.3	0.28
Pb-212	238.6	0.26
Tl-208	583.2	0.42
Ac-228	911.2	0.51
Am-241	59.5	0.13

mum detectable activity MDA has to be determined. In MDA calculations the formula (4) is used, which is in fact a specific case ($t_b >> t_s$) of the generalized Curie formula, proposed by Strom and Stransbury [12]:

$$(4) \qquad MDA = \frac{2.71 + 3.3\sqrt{n_b t_s}}{m t_s \varepsilon p}$$

where: MDA is the minimum detectable activity expressed in Bq/kg, m is the sample mass, t_b, t_s is the time of background measurement and sample measurement (i.e. the time for which the detection limit is to be determined), n_b is the background count rate for the analyzed sample within the region of the considered line; in the definition of MDA the background means both the lines present in the background and Compton continuum, which mostly comes from the sample; width of the line region in n_b calculations is taken as 1.2 FWHM [2].

MDA was computed for water matrix, practically free of radionuclides; detection limit for water defines the minimum limit to be achieved by the system. MDA values for the measurement time 100 h, for several nuclides widely encountered in environmental samples are summarized in Table 3. MDA values are presented for this nuclide line where MDA is the lowest and hence determines the nuclide detection limit.

efficiency and energy $\varepsilon(E)$, $\varepsilon_t(E)$ for particular points in the sample (i.e. the relationships $\varepsilon(E,\boldsymbol{r})$, $\varepsilon_t(E,\boldsymbol{r})$) [2].

Correction factors C_c for the water matrix are calculated using the ETNA program [11]. The input data are: $\varepsilon_{ref}(E)$, $\varepsilon_{t,ref}(E)$ relationships for any reference geometry (e.g. the measurement geometry), a precise description of the measurement geometry and nuclear data of the analyzed nuclide. The program then finds the relationships $\varepsilon(E,\boldsymbol{r})$, $\varepsilon_t(E,\boldsymbol{r})$ and performs the integration procedure to find C_c. Computation results are summarized in Table 2, providing C_c values for the selected lines of artificial nuclides, widely encountered in spectrometry. Uncertainty does not exceed 2÷3% for the correction factor C_c values below 1.25 and still decrease with further decrease of the correction factor.

Detection limit

In order to determine the potential applications of a spectrometer in low-activity measurements the mini-

Verification of the method

The developed methodology, including the determination of efficiency curve and correction factors C_c, C_s were repeatedly verified through measurements of reference materials and through successful participation in intercomparison measurements, involving identification and determination of nuclide concentration and its uncertainty. Concentrations of artificial nuclides obtained in the course of repeated intercomparison measurements differ from the reference values by 2÷7% (average 3%).

Table 4 shows the selected measurement data for the reference materials supplied by the International Atomic Energy Agency (AQCS IAEA): Soil-6 and a spiked coal ash (AQCS IAEA Proficiency Test), containing artificial radionuclides that are the subject to coincidence summing effect.

Table 4. Results of selected measurements verifying the presented methodology. Measurements were carried out in the cylindrical geometry 121 cm^3

Reference sample	Nuclide	Reference nuclide concentration (Bq/kg)	Measured nuclide concentration (Bq/kg)	Bias (%)
AQCS IAEA Soil-6	Cs-137	53.7(16)	51.3(12)	−4.4
	Ra-226	79.9(60)	79.0(13)	−1.1
	Mn-54	36.5(92)	38.0(11)	+4.2
	Co-57	33.9(87)	36.4(18)	+7.3
AQCS IAEA Spiked coal ash	Co-60	145(4)	143.6(28)	−0.7
	Zn-65	23.0(71)	22.8(10)	−0.7
	Y-88	34.9(9)	35.0(11)	+0.4
	Cs-134	76(2)	72.6(29)	−4.0
	Cs-137	160(5)	157.6(32)	−1.5
	Am-241	64(2)	67.5(20)	+5.4

Conclusions

The full methodology was developed for measuring radionuclide activity concentration in the environmental samples by the gamma-ray spectrometry method. This methodology enables high-precision measurements, with a typical uncertainty below 5%. Self-absorption and coincidence summing correction factors C_s and C_c can be determined with uncertainty of the order of several percent. The methodology was successfully verified in the course of repeated intercomparison measurements.

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