Research Article

Validation of gamma-ray spectrometry (GRS) for radionuclides analysis of environmental and food samples

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Abstract
The validation of the experimental methodology, employed at the Laboratory of Environmental Radioactivity of the Environmental Protection Agency of Calabria, Italy to determine the presence of gamma-emitting radionuclides in environmental and food samples, is reported in the present study. The validation process aims to demonstrate the validity of a method for its use by verifying that the requirements that the laboratory aims to achieve are met. High purity germanium spectrometry was employed to determine activity concentrations in certified reference materials obtained from the international atomic energy agency, with the aim to verify the linearity, repeatability, accuracy, trueness and detection limit of the methodology. Investigated radionuclides were ^{137}Cs, ^{40}K, ^{228}Ac and ^{212}Pb. The setup was calibrated using standard sources. Obtained results demonstrate the adequacy of the procedure under consideration; they also document the competence of the operator and provide sufficient data to define the control limits useful for ensuring the quality of the data.

Keywords Gamma-ray spectrometry · Environmental samples · Food samples · Linearity · Repeatability · Accuracy · Trueness · Detection limit

1 Introduction

The presence of cosmogenic and primordial radionuclides in the Earth's crust is the main source of environmental radioactivity [1]; the first ones are produced by the interaction of cosmic rays with atomic nuclei in the atmosphere, while the origin of primordial radioisotopes goes back to the creation of the material, from which the Earth's crust was formed, by the process of nucleo-synthesis [2].

Major sources of natural radionuclides in soil, for example, are weathering and recycling of terrestrial minerals and rocks containing ^{40}K and radioisotopes of the ^{238}U and ^{232}Th radioactive decay chains, rainfall and other depositional phenomena [3]. Airborne particulate matter, otherwise, consisting of a wide class of chemically and physically different elements and compounds, various in sizes, chemical compositions, formations, sources and concentrations, across space and time, is investigated in terms of ^{137}Cs, ^{7}Be and ^{210}Pb radionuclides to evaluate its radioactivity content [4].

Regarding to the radioisotope concentrations, a wide variety of food of animal and vegetable origin can be found where their ingestion constitutes an important pathway by which natural radionuclides can be transferred to humans. The natural radioactivity comes mainly from ^{40}K; uranium and thorium daughter products are usually present in traces [5].

The increasing interest in the determination of radionuclides content in environmental and food makes necessary to investigate the setup used for radioisotope detection, to prevent wrong measurement results of their activity concentrations. Validation of analytical methods is a subject of considerable interest and it is the process of determining the suitability of methodology for providing useful

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analytical data [6]. The data obtained in the validation procedure are useful to evaluate the uncertainty associated with measurements [7].

In this paper the focus was to validate the gamma-ray spectrometry (GRS) with high purity germanium detector (HPGe) methodology, according to the UNI 11665:2017 [8], by using two point sources (^{60}Co and ^{137}Cs) and three standard reference materials (SRMs, IAEA-330 spinach, IAEA-447 moss soil and IAEA-443 Irish sea water) [9, 10].

2 Materials and methods

2.1 Setup

The experimental setup is composed by two Ortec HPGe detectors and integrated digital electronics. The first is a negative biased detector (GMX) with FWHM of 1.94 keV, peak to Compton ratio of 65:1 and relative efficiency of 37.5% at 1.33 MeV (^{60}Co). The second one is a positive biased detector (GEM) with FWHM of 1.85 keV, peak to Compton ratio of 64:1 and relative efficiency of 40% at 1.33 MeV (^{60}Co).

Detectors are placed inside lead wells to shield the background radiation environment. The total count rate within the useful energy range of the spectrometer is of about 5–6 cps; the count rate in the peak at 661.66 keV is of 0.01 cps.

The Gamma Vision (Ortec) software is used for data acquisition and analysis [11]. In particular an appropriate library containing key information (energy, half-life, etc.) about the radionuclides present in the investigated samples is employed to identify them in the spectrum and then to perform activity concentration calculations and decay time corrections [12].

The efficiency and energy calibrations were performed using Eckert and Zigler Nuclitec GmgH traceable multinuclide radioactive standards, number AK 5901, covering the energy range 59.54–1836 keV, customized to reproduce the exact geometries of samples in a water-equivalent epoxy resin matrix [13].

The measurement result uncertainty is a combined standard one at coverage factor $k = 2$, taking into account the following components: uncertainty of the counting estimation, defined as the uncertainty in the gross area and the uncertainty in the background added in quadrature; of the efficiency calibration, depending on the type of fit used for the efficiency calculations; of the γ-branching ratio, defined as the uncertainty in the yield (branching ratio) for the first gamma ray in the library for each nuclide; of the sample holder geometry, referred to the variability of the analysis geometry; of the instrumental response oscillation, referred to the variability of the spectrometric chains response; and of any contributions of self-absorption and true coincidence correction (TCC) [13].

2.2 Linearity

To verify the linearity of the instrumental response, for a HPGe detector, the ratio of the absolute germanium detector efficiency to the efficiency of a 3″ × 3″ NaI(Tl) scintillation detector at 25 cm (known to be 1.2×10^{-3}), ε_r, was evaluated at the ^{60}Co peak at 1.33 MeV, by varying the total count rate [14].

A point source of ^{60}Co (Eckert & Ziegler AC-8286) was fixed at 25 cm from the detector and the total count rate was changed by positioning another point source of ^{137}Cs (Amersham Buchler GmbH & Co KG CE-746) at different distances from the detector (0, 5, 10, 15 and 20 cm, respectively) [15]. Their geometric and physical features are reported in Table 1.

The measurement time was chosen so as to obtain, by changing the relative distances between the point sources, the same statistical counting uncertainty on the net area of the ^{60}Co peak at 1.33 MeV [16].

2.3 Repeatability

The repeatability of the measurement process was evaluated by means of replicate analysis (10 times) of a certified sample of spinach (IAEA-330), in a 20 ml vial geometry, by measuring the ^{137}Cs and ^{40}K activity concentrations under repeatable conditions [17].

The standard deviation (%) was evaluated and compared with the statistical counting uncertainty (at $\sigma = 1$) by means of the Fisher test [18]. If the first one is significantly different from the second one, so it represents an estimation of the methodology repeatability and it has to be taken into account in the evaluation of the total measurement uncertainty [19].

The standard deviation is also used to calculate the limit of repeatability, given by [20]:

Table 1 Geometric and physical features of the ^{60}Co and ^{137}Cs point sources

Code	Geometry	Nuclide	$T_{1/2}$ (y)	Activity, T_0 (Bq)	Reference date, T_0
AC8286	Point source	Co-60	5.27	37,800	09/01/2013
CE746	Point source	Cs-137	30.07	33,900	10/01/1990

$$r = \sqrt{2} \cdot t_{p=95\%,v=n-1} \cdot s \quad (1)$$

where $t_{p=95\%,v=n-1}$ is the value of the Student's *t* distribution evaluated at the 95% probability level as a function of the number of degrees of freedom (v = n − 1 = 10 − 1 = 9) (2.26) and *s* is the standard deviation of the results distribution (%).

This limit is very useful for the double tests, performed by using the same SRM used to estimate the repeatability of the method (IAEA-330) [21].

2.4 Accuracy

The accuracy of the methodology was verified by measuring the SRMs activity concentration (^{137}Cs and ^{40}K for the IAEA-330 spinach (in a 20 ml vial) and IAEA-443 Irish sea water (in 1 l Marinelli beaker), ^{137}Cs, ^{40}K, ^{228}Ac and ^{212}Pb for the IAEA-447 moss soil (in a 20 ml vial), respectively), according to the criterion of acceptability given by [22]:

$$u_{test} = \frac{measured\ value - reference\ value}{\sqrt{u_{meas}^2 + u_{ref}^2}} \leq 2 \quad (2)$$

where u_{meas}^2 is the total measured uncertainty and u_{ref}^2 that one reported for the SRMs.

2.5 Trueness

The trueness of the measurement results, defined as the agreement degree between the average value of ten IAEA-330 experimental specific activity measurements and the reference one, was evaluated, thus verifying if their difference is significant or not at the 95% of confidence with the following [23]:

$$\frac{|C_{SRM} - m|}{\sqrt{\frac{s_r^2}{n} + u_{SRM}^2}} \leq t_{p,v} \quad (3)$$

where C_{SRM} is the radioisotope activity concentration for the reference material, *m* the average value of IAEA-330 experimental specific activity measurements, s_r the standard deviation, *n* the number of measurements, u_{SRM} the uncertainty of the certified specific activities and $t_{p,v}$ the Student coefficient at a 95% probability level, for v = n − 1 = 9 degrees of freedom (2.26) [24].

2.6 Detection limit

The detection limit was verified for ^{134}Cs and ^{137}Cs by using a sample of underground water for human use in Marinelli geometry (1 l), with 70,000 s. as measurement time.

Obtained values were compared with those reported in the UNI 11665:2017 Appendix C [8].

3 Results and discussion

The verification of the linearity for HPGe detectors GMX and GEM is reported in Table 2a and b, respectively. The relative efficiency, $\varepsilon_{r,\ Co\text{-}60}$, linearly varies with the total count rate, in the range of counting rates of GMX and GEM, respectively, as verified through the ANOVA test with the total count rate values as input parameters [25]; so, the instrumental response is linear with respect to the input signal [26].

The evaluation of the repeatability for HPGe GMX and GEM is reported in Tables 3a and b, respectively. For both detectors, for v = 9 degrees of freedom, the Fischer's random variable F is 3.18 [18]. So, the standard deviation (%) is significantly different from the statistical counting uncertainty (at σ = 1) for ^{137}Cs; their ratio (3.81 and 3.67 for GMX and GEM, respectively) is in fact greater than F and then the standard deviation is not completely explained by the statistical counting uncertainty. Otherwise, for ^{40}K,

Table 2 Linearity verification results for HPGe detectors GMX and GEM

d (^{137}Cs-detector) (cm)	$\varepsilon_{r,\ Co\text{-}60}$ (%)	Total count rate (cps)	Dead time (%)	Live time (s.)
GMX Detector				
0	38.2 ± 0.4	996.4	14.41	1167
5	39.6 ± 0.4	161.4	3.11	1167
10	41.1 ± 0.4	73.8	1.89	1167
15	40.8 ± 0.4	44.5	1.49	1167
20	41.6 ± 0.4	31.7	1.29	1167
GEM Detector				
0	35.2 ± 0.4	926.9	9.94	1167
5	35.4 ± 0.4	150.6	2.07	1167
10	35.8 ± 0.4	64.3	1.16	1167
15	36.1 ± 0.4	38.5	0.88	1167
20	35.4 ± 0.4	26.9	0.75	1167

Table 3 The evaluation of the repeatability for HPGe GMX and GEM

N	^{137}Cs activity concentration (Bq/kg)	Uncertainty (σ = 1) (%)	^{40}K activity concentration (Bq/kg)	Uncertainty (σ = 1) (%)
GMX Detector				
1	1074	0.73	1081	6.1
2	1042	0.68	1112	5 4
3	1098	0.69	1145	5.8
4	1113	0.73	1215	5.8
5	1076	0.70	980	6.5
6	1138	0.72	1188	5.9
7	1091	0.72	1227	5.6
8	1057	0.69	1075	5.6
9	1115	0.74	1111	6.3
10	1112	0.72	1119	6.1
Average	1091.6	*0.71*	1125	*5.9*
Standard deviation (%)	*2.7*	2.9	*6.5*	5.7
GEM Detector				
1	1216	0.77	1367	5.7
2	1233	0.79	1282	6.2
3	1166	0.77	1281	5.7
4	1227	0.81	1283	6.5
5	1147	0.82	1106	7.2
6	1185	0.81	1213	6.6
7	1192	0.79	1167	6.6
8	1136	0.77	1164	6.0
9	1219	0.76	1258	6.1
10	1212	0.83	1266	6.5
Average	1193	*0.79*	1239	*6.3*
Standard deviation (%)	*2.9*	*3.0*	*6.1*	*7.1*

GMX Detector: a negative biased High Purity Germanium (HPGe) Ortec detector, model named GMX
GEM Detector: a positive biased High Purity Germanium (HPGe) Ortec detector, model named GEM

Table 4 The verification of the accuracy for HPGe detectors GMX and GEM

Sample	Radio nuclide	Measured value (Bq/kg)	U_{mass} (k = I)	Reference value (Bq/kg)	U_{ref} (k = I)	U_{test}
GMX Detector						
IAEA-330	Cs-137	1138	59	1235	17	−1.6
IAEA-330	K-40	1187	92	1188	15	−0.01
IAEA-447	Cs-137	406	20	425	10	−0.8
IAEA-447	K-40	499	64	550	20	−0.8
IAEA-447	Ac-228	29	7.1	37	2.0	−1.1
IAEA-447	Pb-212	33	3.1	37	2.0	−1.1
IAEA-443	Cs-137	0.48	0.08	0.36	0.01	15
IAEA-443	K-40	11.7	1.7	11.4	0.2	0.2
GEM Detector						
IAEA-330	Cs-137	1257	66	1235	17	0.3
IAEA-330	K-40	1191	171	1188	15	0.02
IAEA-447	Cs-137	439	21	425	10	0.6
IAEA-447	K-40	588	75	550	20	0.5
IAEA-447	Ac-228	46	7.7	37	2.0	1.2
IAEA-447	Pb-212	41	3.7	37	2.0	1.1
IAEA-443	Cs-137	0.36	0.04	0.36	0.01	0.1
IAEA-443	K-40	9.8	1.2	11.4	0.2	−1.3

Table 5 The trueness evaluation for GMX and GEM

	^{40}K $C_{SRM} \pm u_{SRM} = 1188 \pm 15$ (Bqkg)
N	Experimental activity concentration (Bq kg)
GMX Detector	
1	1081
2	1112
3	1145
4	1215
5	980
6	1188
7	1227
8	1075
9	1111
10	1119
Average, m	1125
Standard deviation, s_r	73.6
GEM Detector	
1	1367
2	1282
3	1281
4	1283
5	1106
6	1213
7	1167
8	1164
9	1258
10	1266
Average, m	1239
Standard deviation, s_r	71.4

the standard deviation (%) is not significantly different from the statistical counting uncertainty (at σ = 1) because their ratio (1.10 and 0.97 for GMX and GEM, respectively) is lower than F; the first one, then, is totally explained by the second one.

From all these results we can then evaluate a repeatability of 2.7% and 2.9% for HPGe GMX and GEM, respectively. Moreover, the limit of repeatability calculated with Eq. (1) is 93.9 Bq/kg and 119 Bq/kg for GMX and GEM, respectively.

The verification of the accuracy for HPGe detectors GMX and GEM is reported in Tables 4a and b, respectively. All measured values satisfy the criterion of acceptability given by Eq. (2).

For radiometric measurements, where the absolute uncertainty is routinely calculated using the metrological approach [13] and not as standard deviation, the trueness evaluation is not mandatory for a standardized method like ours [27]. We verified it for a significative radionuclide in the routine analysis, ^{40}K, for which no systematic effects are present [28]. In our validation, $C_{SRM} \pm u_{SRM} = 1188 \pm 15$ (Bq/kg) for this natural radioisotope. For other radionuclides like as ^{137}Cs, the uncertainties cover the systematic effects, so that the accuracy can be considered acceptable [27]. Obtained results are shown in Tables 5a and b for GMX and GEM, respectively. The ratio given by Eq. (3) is 2.01 for GMX and 1.35 for GEM, respectively; in both cases, it is lower than 2.26 and then the criterion of trueness is satisfied.

Table 6 The detection limit verification for GMX and GEM

Radionuclide	Detection limit (Bq/kg)
GMX Detector	
^{137}Cs	0.072
^{134}Cs	0.088
GEM Detector	
^{137}Cs	0.086
^{134}Cs	0.088

The detection limit verification results are reported in Tables 6a and b for GMX and GEM, respectively. They are in very good agreement with those reported in the UNI 11665:2017 Appendix C (0.1 Bq/kg for ^{134}Cs and ^{137}Cs).

4 Conclusions

This work investigates the validation of GRS methodology at the Laboratory of Environmental Radioactivity of the Environmental Protection Agency of Calabria, Department of Reggio Calabria, Italy, by determining the presence of gamma-emitting radionuclides in different matrices.

The linearity, repeatability, accuracy, trueness and detection limit of the methodology were tested. They were verified and evaluated according to the UNI 11665:2017. Obtained results shows that GRS analytical method can be used to quantify the activity concentration of gamma-emitting radioisotopes in environmental and food samples.

Compliance with ethical standards

Conflict of interest The authors declare that they have no financial conflict of interest in the subject matter or materials discussed in this manuscript.

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