LOW LEVEL RADIOACTIVITY MEASUREMENTS OF ^{238}U, ^{232}Th, ^{40}K AND $^{134, 137}$Cs IN THE ENVIRONMENTAL AND INDUSTRIAL SAMPLES BY HIGH RESOLUTION GAMMA-RAY SPECTROMETRY

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Abstract

In recent years, low level radioactivity measurements of radionuclides, especially the long-lived radionuclide ^{137}Cs ($t_{1/2}$=30.1 y) in the environmental samples have an increasing importance due to the global fallout originating from atmospheric contamination caused by nuclear weapon tests and nuclear accidents (after Chernobly accident). In addition, a need has arisen to find and produce materials containing low in radioactive promordial elements thorium, uranium and potassium since these materials, in particular, cement, clays and ash fly from the coal-fired thermic power plants are widely used in several mass-production industrial applications such as for the making concrete, bricks, seramics.

In this work, the radioactivity measurements of ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K, ^{134,137}Cs and other radionuclides in environmental and industrial samples such as soil, coal, ash fly, cement, etc. were measured routinely by using high resolution gamma-ray spectrometry, after a method validation by IAEA proficiency tests within a QA/QC program by IAEA RER/2/004 project, in Ankara Nuclear Research and Training Center in Turkey. The gamma-spectrometric method employed is described and the analysis results for various samples are given in this paper.

1. Introduction

More than 40 years after its launching, the gamma-ray spectrometry with especially high pure Germanium detectors developed in the last 30 years, is nowadays applied to measure quantitatively gamma emitting radionuclides for various research purposes and environmental problems in numerous laboratories world-wide. Since the gamma-ray spectrometry is a non-destructive and fast analytical technique and it gives the high accuracy and precision in the results, this technique is commonly used in measurements of the low level radioactivity contained various samples, e.g., rock, soil, sediments, sludge, mineral ores, cement, seramics, clays and petroleum industry. Particularly, in areas of igneous geology, the measurements of concentrations of naturally occuring U, Th series nuclides and ^{40}K are significant [1]. Additionaly, a need has recently arisen to find and produce

materials containing especially low in radioactive promordial elements thorium, uranium and potassium [2].

The comparator (i.e, relative) method for radioactivity measurements in samples is straightforward if the standard materials are similar to the samples, especially in view of matrix composition. However, it is difficult to obtain such suitable standard materials. Therefore, the direct (or absolute) gamma spectrometric method for radionuclide analysis in samples is generally applied in a calibrated Ge detector.

In this work, the gamma emitting radionuclides in the spiked soil samples and standard solutions prepared by IAEA for proficiency tests have been analysed by using a gamma-ray spectrometer with a n-type detector within the quality control and quality assurance of the employed technique at ANRTC. The obtained results (i.e., the results reported to IAEA) for proficiency test samples sent by IAEA were compared with the IAEA data by using statistical methods (z-score and u-test score). In this paper, the gamma-ray measuring system and experimental procedure used have been described in detail and the results obtained by absolute gamma-spectrometric method and the target values (IAEA measurements) and their uncertainties have been discussed for the validation of method in view of the proficiency test. Then, the analysis results for various environmental and industrial samples are given.

2. Experimental Procedure

For gamma spectrometric measurements, two p-type and one n-type Ge dedectors are being routinaly used at ANRTC. The gamma measuring system consisting of a commercially available n-type Ge detector (reverse electrode germanium crystal, REGe) with its own preamplifier, a spectroscopy amplifier, a 100 MHz- Wilkinson type ADC and a multichannel analyzer (Canberra Model 95+) is described here as an example for me gamma-ray spectrometers used in the measurements. The REGe detector has a total active volume of 100 cm^3 and 0.5 mm thick Be window. So, it has high efficiencies for low energy gamma-rays (< 120 keV). The REGe detector has a relative efficiency of 22.6% and its measured resolution is 1.80 keV for 1332.5 keV (^{60}Co) and 0.97 keV for 122 keV (^{57}Co). The detector was shielded by chevron type lead bricks with 10 cm thickness. The lead gamma shielding of the detector was lined with 1 mm thick Cu sheets to reduce Pb-rays.

The full-energy detection efficiency as a function of gamma-ray energy for the REGe detector was determined using the powder radioactive standard containing a mixture of ^{109}Cd, ^{57}Co, ^{123m}Te, ^{51}Cr, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{60}Co and ^{88}Y in SiO_2 matrix and a 5 ml ampoule containing radionuclides ^{57}Co, ^{60}Co, ^{88}Y, ^{109}Cd, ^{113}Sn, ^{137}Cs from the Isotope Products Laboratories Inc traceable to NIST.

The measured absolute photopeak efficiency data at a desired and reproducible source to detector distance are fitted using the least square fitting method to an efficiency function in the following form:

$$\varepsilon_p\left(E_\gamma\right) = a + b\exp(-cE_\gamma^d) \quad (1)$$

where, ε_p: absolute photopeak efficiency as a function of gamma-ray energy, E_γ and a, b, c and d are constants determined by the fitting method.

For a given source sample geometry, the weighed spiked soil samples coded as RER/2/004/TU-ANK/1 and RER/2/004/TU-ANK/14, and standard solutions coded as RER/2/004/TU-ANK/2 and RER/2/004/TU-ANK/15 were counted in a calibrated REGe detector for different counting times of 100 000 s, 150 000 s and 235 000 s according to the level of activity of the sample to ensure good statistical quality of data. The measurements for each sample were repeated at least three times to improve statistical precision. Thus, the mean values of the measured count rates were used in the calculations. In peak analysis procedure, as is known, there are many ways of calculating the net gamma ray count. The employed here is valid, common method when there are no interference from photopeaks adjacent to the peak of interest. In case of the interference gamma peaks from the radionuclides that may be contained in sample and/or ambient background, a peak deconvolation method (e.g. Gauss Fitting Deconvolation Method) is applied to separate the adjacent peaks.

Since the series Canberra 95+ MCA used has advanced functions, the full energy peak areas are determined by appliying automatic computation. Nevertheless, some full energy peak areas are often checked by manual selection. The areas determined by two ways did not differ more than 0.1%. Also, the background spectrum was separately collected several times for the different periods. The background peak areas were converted to count rates and then the average value from the background runs were substracted from photopeak count rates to obtain the net sample count rate for each photopeak of interest. In these measurements the laboratory background values were checked by using control chart of background. They remained within $\pm 1\sigma$ (standard deviation) levels of the control chart for this detector. The specific activity of any radionuclide in the sample using net counts of the peak of interest in the measured spectrum was calculated by the following formula:

$$A = \frac{N_p / t_c}{f_\gamma \varepsilon_p D w} \quad (2)$$

where, N_p: net counts for the peak of interest, t_c: the counting time (sec.), A is the specific activity in $Bq \cdot g^{-1}$, w: sample weight (g), f_γ:gamma emission probability per decay, ε_p: full energy peak efficiency for a given energy E_γ, D: decay correction factor [=exp(-0.693 t/ $T_{1/2}$)] in which t is decay time from reference date of

standard to start of MCA and $T_{1/2}$= radionuclide half- life. For short life radionuclides, the correction for the decay for a period of measurement was also made. The lowest detectable activity level in Bq/g for the peak region of interest at the 90% confidence level is calculated by the following Curie' s formula [3]:

$$MDA(Bq/g) = \frac{2.75 + 4.66\sqrt{N_{bkg}}}{t_c \varepsilon_p f_\gamma w} \quad (3)$$

where, MDA is the minumum detectable activity per unit weight (Bq/g), N_{bkg} is the background count collected during time t_c for the peak of interest, t_c is the counting time (sec.), ε_p, f_γ and w are the same as in Eq. 2.

3. Results and Discussion

The measured results and IAEA data for one of two spiked soil samples (TU-ANK/1 and TU-ANK/14) and one of the standard solutions (TU-ANK/2 and TU-ANK/15) are given Table 1 and in Table 2 to evaluate proficiency test results for the gamma spectrometric technique used in ANRTC. It is seen from Table 1 and 2 that most of the measured results are consistent with the target values (i.e., IAEA data). The uncertainty sources for activity calculation in Eq (2) are:

1) The accuracy of the gamma emission yields and isotope half-lives taken from NUDAT database [4] and Tuli's wallet card [5].
2) The accuracy of the sample weight determination (±0.1 mg, balance accuracy)
3) The uncertainty in the counting statistics of the peak area, σ_p for each photopeak can be expressed as the percent error= $(m\sigma_p/N_p)\cdot 100$. Where, σ_p= the net peak area uncertainty, N_p= net area of the peak region of interest and the factor , m= 1.65 at 90% confidence level.
4) The uncertainty of absolute efficiency (full energy photopeak efficiency) of detector is determined from the calibration curve in which the uncertainties of the radioactive standard sources (the uncertainties of the certified activities are in order of ±3%) are taken into account the measured efficiency values.

The final combined uncertainty for each radionuclide activity is expressed as the square root of the sum of variances by using normal error propagation law.

The difference between the measured value (the reported value) and the target value (the IAEA value) for each radionuclide given in Table 1 and Table 2 is described using three parameters: the relative bias, the z-score value and the value of u- test score.

Table 1. The activity values measured in ANRTC and IAEA data for the soils spiked with the gamma-emitting radionuclides.

Sample Unit Code (Bq/g)	IAEA data Value	Unc.	Our results (Reported results) Value	Unc.	Rel. Bias [%]	Z-test score	u-test score
^{57}Co	37.8	0.92	36.84	0.82	-2.53	-0.16	0.74
^{60}Co	93.5	1.61	89.52	2.24	-4.26	-0.28	1.44
^{65}Zn	29.5	1.28	26.00	2.77	-11.7	-0.78	1.13
^{134}Cs	73.0	1.47	74.21	2.23	1.68	0.11	0.46
^{137}Cs	84.2	1.79	86.55	1.71	2.80	0.19	0.95
^{241}Am	93.1	7.50	82.88	1.39	-11.0	-0.73	1.34

The spiked soil sample: RER/2/004/TU-ANK/1, Ref. Date:1 Jan. 2000.

Table 2. The activity values measured in ANRTC and IAEA data for the standard solution.

Sample Unit Code (Bq/g)	IAEA data Value	Unc.	Our results (Reported results) Value	Unc.	Rel. Bias [%]	Z-test score	u-test score
^{57}Co	17.04	0.104	18.100	0.056	6.22	0.42	8.95
^{60}Co	16.60	0.070	16.965	0.129	2.19	0.15	2.48
^{65}Zn	10.61	0.192	11.726	0.220	10.5	0.70	3.83
^{134}Cs	6.65	0.034	6.656	0.089	0.11	0.01	0.08
^{137}Cs	21.74	0.328	22.386	0.116	2.99	0.20	1.87
^{241}Am	16.53	0.823	16.629	0.072	0.60	0.04	0.12

The standard solution: RER/2/004/TU-ANK/2, Ref. Date: 1 Jan. 2000

i) The relative bias:
The relative bias between the analyst result and the target value (IAEA data) is expressed as a percentage:

$$\mathrm{Re}l.bias = (Value_{Analyst} - Value_{IAEA}) \times 100 / Value_{IAEA} \quad (4)$$

ii) The z- score value:
The z- score value is calculated according to the following equation:

$$z_{score} = (Value_{Analyst} - Value_{IAEA}) / \sigma \quad (5)$$

where the target value for standard deviation (σ) equals $0.15 \times \mathrm{Value}_{\mathrm{IAEA}}$ for all standard solutions and soil samples spiked with gamma emitting radionuclides.
iii) The u- test score value:
The value of the u- test score for each radionuclide is calculated as follows [6]:

$$u - testscore = \left| Value_{IAEA} - Value_{Analyst} \right| / \left[Unc_{IAEA}^2 + Unc_{Analyst}^2 \right]^{1/2} \quad (6)$$

where "Unc" means the uncertainty of a value.
The calculated u- test value can be compared with critical values listed in the t-statistic tables. It is known that the choice of signifance level at a given level of probability is subjective. If the reported value (i. e. analyst's result) differs significantly from the expected value (IAEA data) at a given probability (< 0.001) in t- statistic tables, the limiting value for the u- test parameter for this proficiency test can be set as the condition 3.29 to determine whether a result passes the u- test (i. e., condition u≤ 3.29).
The accuracy and precision of the measured values for the activities of radionuclides contained in the spiked soil and the standard solutions were determined according to the following expressions:

1) Accuracy: the measured value is assigned the status "passed" if,

$$\left|Value_{IAEA} - Value_{Analyst}\right| \le 3.29 \times \sqrt{Unc_{IAEA}^2 + Unc_{Analyst}^2} \tag{7}$$

and,

2) Precision (dependent on the activity level): the measured result is assigned the status "passed" if,

$$\left[\left(\frac{Unc_{IAEA}}{Value_{IAEA}}\right)^2 + \left(\frac{Unc_{Analyst}}{Value_{Analyst}}\right)^2\right]^{1/2} \times 100 \tag{8}$$

is ≤ 15% for the spiked sample and standard solutions containing gamma emitting radionuclides.
The measured values and their uncertainties were evaluated against the above acceptance criteria for accuracy and precision assigned the status "passed" or "rejected". A result must pass both criteria (accuracy and precision) to be assigned final status of "passed".

Table 3. The accuracy and the precision criteria and final status for the spiked soil sample.

Radio-nuclide	Accuracy criteria $\left\|Value_{IAEA} - Value_{Analyst}\right\| \le 3.29\sqrt{Unc_{IAEA}^2 + Unc_{Analyst}^2}$		Status	Prec. Criteria [%]	Status	Final status
^{57}Co	0.92	4.06	P	3.3	P	P
^{60}Co	3.98	9.08	P	3.0	P	P
^{65}Zn	3.45	10.0	P	11.5	P	P
^{134}Cs	1.23	8.79	P	3.6	P	P
^{137}Cs	2.35	8.15	P	2.9	P	P
^{241}Am	10.2	25.1	P	8.2	P	P

The spiked soil sample: Code RER/2/004/TU-ANK/1
The accuracy and precision criteria and the final status for the spiked soil samples and standard solutions are given in Table 3 and in Table 4.

The number of final status for two spiked soils and two standard solutions are 22. The result for ^{54}Mn in the spiked soil No: 2 and the result for ^{152}Eu in the standard solution No: 2 in Table 3 were not reported to IAEA because these radionuclides were less than their minimum detectable activities for the present measuring system. The number of final status "rejected" is only four. In other words, 16 of the 20 reported results have had the final status "passed" for two proficiency tests. One of the main reasons for the failed results is the delay (3 to 6 months) in the arrival time of the samples to the laboratory. The decay of the radionuclides in the delay time affected directly the counting statistics. However the success of the proficiency test results for γ-spectrometry within RER project, QA/QC of the analytical techniques is 80%.

Table 4. The accuracy and precision criteria and final status for the standard solution.

Radio-nuclide	Accuracy criteria $\lvert Value_{IAEA} - Value_{Analyst} \rvert \leq \leq 3.29\sqrt{Unc^2_{IAEA} + Unc^2_{Analyst}}$		Status	Prec. Criteria [%]	Status	Final status
^{57}Co	1.06	0.39	F	0.7	P	R
^{60}Co	0.36	0.48	P	0.9	P	P
^{65}Zn	1.12	0.96	F	2.6	P	R
^{134}Cs	0.01	0.31	P	1.4	P	P
^{137}Cs	0.65	1.14	P	1.6	P	P
^{241}Am	0.10	2.72	P	5.0	P	P

The standard solution: Code RER/2/004/TU-ANK/2
P: Passed, F: Failed, R: Rejected.

The radioactivities measured in soil, fly ash and cement samples. The samples were sent to the laboratory from different origins by customers to obtain an analysis certificate. The soils of Bosnia Hertzegovina were sent to Turkey by Turkish Army Forces, after the speculation of the depleted uranium bombs used in Bosnia. The other samples from Turkey are related to the use of fly ash produced in coal-fired thermic power plants in making concrete and brick. In near future, the analysis of α-emmiting radionuclides in samples will be carried out routinely at ANRTC by using an Alpha Analyst with 8 PIPS dedectors, recently purchased by Canberra Inc.

Table 5. The activities measured in soil, fly ash and cement samples.

Sample No	Sampling Origin (Sample Type)	The measured activity (Bq/kg) U-238 Ra-226	Th-232	K-40	Cs-137
1	Bosnia Hertzegovina(Soil)	27,2 ± 3,2	10,5 ± 1,9	507 ± 33	< MDA
2		30,0 ± 2,1	11,1 ± 1,5	584 ± 26	< MDA
3		16,2 ± 2,1	11,5 ± 2,1	696 ± 38	< MDA
4		18,1 ± 1,4	8,0 ± 1,1	297 ± 16	< MDA
5		24,8 ± 2,7	47 ± 9	683 ± 37	< MDA
6		70 ± 7	37 ± 4	1783 ± 85	111 ± 7
7		32 ± 2	56 ± 8	599 ± 27	8,5 ± 0,9
8		40 ± 4	103 ± 11	1852 ± 61	< MDA
9	Sinop(Soil)	17,3 ± 2,6	43 ± 6	< MDA	51 ± 5
10		23,5 ± 3,5	36 ± 6	< MDA	172 ± 9
11		19,5 ± 2,0	32 ± 8	< MDA	216 ± 6
12		30,2 ± 2,2	29,3 ± 2,7	404 ± 12	90 ± 3
13	Cimentaş (Soma - Fly Ash)	504 ± 6	104 ± 6	399 ± 12	< MDA
14	Cimentaş (Soma - 20% Fly Ash Cement)	29,2 ± 4,5	18,3 ± 3,5	113 ± 5	< MDA
15	Cimentaş (Yatağan - Fly Ash)	520 ± 7	152 ± 7	616 ± 18	< MDA
16		406 ± 8	90 ± 6	670 ± 33	< MDA
17		345 ± 7	104 ± 7	693 ± 36	< MDA
18		418 ± 5	54 ± 3	354 ± 17	< MDA
19		498 ± 10	110 ± 6	729 ± 22	< MDA
20	Cimentaş (Henkel - Fly Ash)	1312 ± 20	624 ± 24	4282 ± 103	< MDA
21	Cimentaş (Soma - 12% Fly Ash)	96 ± 3	38 ± 3	364 ± 16	< MDA
22		88 ± 4	40 ± 4	346 ± 22	< MDA
23		197 ± 5	123 ± 6	339 ± 12	< MDA
24	ARES Çimento(Fly Ash)	102 ± 4	99 ± 7	696 ± 18	< MDA
25		113 ± 5	102 ± 8	629 ± 16	< MDA
26		317 ± 7	149 ± 10	467 ± 13	< MDA
27	Denizli Çimento (Fly Ash)	2321 ± 13	127 ± 13	393 ± 31	< MDA
28		1711 ± 17	70 ± 6	350 ± 14	< MDA
29	Özgür Beton(Cement)	126 ± 5	86 ± 6	332 ± 17	< MDA
30	Denizli Çimento (Cement)	132 ± 3	50 ± 2	379 ± 14	< MDA

MDA: Minimum Detectable Activity.

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