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Determination of the content of natural radionuclides in furnace slag used for the preparation of standard sources

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Abstract We describe the measurement of the activity concentration of natural radionuclides in a slag material intended to be spiked with a standard solution of ^{226}Ra. The final aim was to produce standard sources within a EURAMET-European Metrology Research Program research project (MetroMetal). High resolution gamma-ray spectrometry was performed in five laboratories from Romania and Spain. Results, given in activity concentration, were analyzed using three different modes for the calculation of the mean from individual values. Reference activity concentration values are presented.

Keywords EURAMET-EMRP IND04-MetroMetal · Standard ^{226}Ra · Slag sample · Naturally occurring radionuclides · HPGe gamma-ray spectrometry

Introduction

The measurement of the radioactive content of materials involved in metallurgical industry both as raw and finite products is a matter of concern for all important companies in the area. The reported values, obtained using a large variety of instruments and methods for sampling, processing, measurement of samples and reporting the final results, could be questionable. For this reason, it was proposed that in the frame of the EURAMET-European Metrology Research Program (EMRP) Joint Research Project (JRP) IND 04 "MetroMetal, Ionising Radiation Metrology for the Metallurgical Industry", a set of standard sources of cast steel, slag and dust fume, artificially spiked with standard solutions or with a residual contamination of natural occurring or artificial radionuclides, were prepared. A special problem to be solved is the existing contamination of slag with natural occurring radionuclides, from the ^{238}U, ^{235}U, ^{232}Th series and ^{40}K, which is non negligible and influences the uncertainty in determination of the activity of the standard source. The content of slag is strongly dependent on their occurrence in raw materials used in metallurgy, such as iron ore, coal, auxiliary materials. A systematic study on all implied materials was performed at the Arcelor Mittal Galati SA (former ISPAT SIDEX), Romania, collaborator of the JRP, [1, 2]. They found a high content of activity in used materials: iron ore, ^{238}U daughters—mean activity concentration of ^{226}Ra, 100 Bq kg^{-1}; ^{232}Th daughters—mean ^{212}Pb, ^{212}Bi and ^{228}Ac, 25 Bq kg^{-1}; ^{40}K—300 Bq kg^{-1}, respectively coal—^{226}Ra, 100 Bq kg^{-1}, ^{232}Th daughters—mean ^{212}Pb, ^{212}Bi and ^{228}Ac, 25 Bq kg^{-1}; ^{40}K, 50–100 Bq kg^{-1} and in other measured materials. They also reported mean contents of slag from the company as high as: mean ^{226}Ra—200 Bq kg^{-1}, mean ^{212}Pb, ^{212}Bi and ^{228}Ac—30 Bq kg^{-1} and ^{40}K—150 Bq kg^{-1}. The authors concluded that the slag concentrates the natural radionuclides, while cast steel is almost free from them: less than 20 Bq kg^{-1} for each measured radionuclide. A recent comparison between methods used to measure slag in Arcelor Mittal and IFIN-HH laboratories confirmed the high contents of natural occurring

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radionuclides. Analysis of slag from another source, the CEPROCIM SA Romanian company, indicated lower content of radionuclides from the ^{238}U series, but higher contribution in ^{40}K and ^{232}Th series [3]. This unavoidable content of natural radionuclides in slag is the reason for which two laboratories of the JRP partner IFIN-HH, Radionuclide Metrology Laboratory (RML) and MicroBq (μBq), Romania, and three laboratories of the JRP coordinator center, CIEMAT, Laboratorio de Medidas de Proteccíon Radiológica (LMPR), Laboratorio de Metrología de Radiaciones Ionizantes (LMRI), Laboratorio de Radiactividad Ambiental (LRA), Spain, measured the radionuclide content of samples from the same slag batch, from a Spanish metallurgical company; it will be used to prepare the ^{226}Ra spiked material necessary for the standard sources. The slag was previously processed and fully characterized from physico-chemical point of view at CIEMAT. This paper presents the experimental conditions, measurement methods, individual results and their combination, in order to report the mean activity values and their combined uncertainties, for each identified radionuclide.

Materials and methods

Sample preparation

The black slag was processed and fully characterized from physico-chemical point of view at CIEMAT [4]; its parameters, such as provided to the participants, to be used for the processing of experimental data, are presented in Table 1.

Table 1 Determined parameters of the slag Mejuto et al. [4]

Chemical composition	Mean percentage (%)	Physical parameter	Value
FeO	25	Density	2.150 g cm^{-3} (CIEMAT)
Fe_2O_3	25		2.220 g cm^{-3} (IFIN-HH)
CaO	25	Humidity	2.84 %
CaO free	2		
SiO_2	11		
Al_2O_3	5		
MgO	5		
MnO	5		

Each laboratory received a quantity of material from the same batch of slag and prepared the measurement sample, in its currently used recipients, which were then sealed. Table 2 presents the types of recipients, dimensions and masses of slag in the containers.

Measurement of samples

All laboratories measured the samples by high resolution HPGe gamma-ray spectrometry. Four partners performed the measurements in laboratories situated at the ground level, while the fifth one, IFIN-HH μBq laboratory, is situated in the Unirea former salt mine, at a floor depth 208 m from the surface entrance [5]. All laboratories had previous experience in the measurement of low activity concentrations; IFIN-HH-RML participated in the past at various international comparisons regarding the measurement of low activity concentration of samples containing artificial or naturally occurring radionuclides and their equipment and methods have been previously described [6–8]. Similar information concerning measurement equipment and methods in use at CIEMAT laboratories can also be found in previous publications [9–11]. Figure 1 presents a photograph of the laboratory and of the HPGe detection system.

Table 3 summarizes the equipment of the participant laboratories, including the main characteristics of the detector and electronics, the software used for acquisition and data processing, the system calibration conditions and typical counting times.

The measurements were done for long counting times. At IFIN-HH the counting time varied from 28,800 up to 261,000 s for RML and μBq laboratories, both for background and sample; the background counting rates in the full absorption peak (FAP) energy of 609 keV were 0.47 cpm, respectively 0.023 cpm. The sample was measured in condition of almost secular equilibrium between ^{226}Ra and ^{222}Rn. The latter approach was followed by one laboratory (LRA) at CIEMAT, while the other two measured in conditions of prompt and secular equilibrium Typical counting times varied from 60,000 to 230,000 s.

In these conditions, the activities of samples, except ^{235}U, were much higher than the minimum detectable activity

Table 2 Description of measurement samples

Laboratory	IFIN-HH, μBq	IFIN-HH, RML	CIEMAT, LMRI	CIEMAT, LMPR	CIEMAT, LRA
Container					
Material dimensions, ($\Phi \times h$) cm	Polypropylene cylindrical (7.5 × 3) cm	Polypropylene cylindrical (7.5 × 3) cm	Polypropylene cylindrical (7.5 × 3) cm	Polypropylene cylindrical (7.5 × 3) cm	Polypropylene cylindrical (7.5 × 3) cm
Mass of slag in sample (g)	200	200	160 and 200	200	100

Fig. 1 **a** The external view of the μBq laboratory. **b** The HPGE detection system

Table 3 Equipment characteristics, software and calibration conditions

Laboratory	IFIN-HH, μBq	IFIN-HH, RML	CIEMAT, LMRI	CIEMAT, LMPR	CIEMAT, LRA
Detector					
Type	Coaxial open end	Coaxial GEM	Extended range	Broad energy	Extended range
Window	Al (1 mm)	Al (1 mm)	Carbon-epoxy (0.5 mm)	Carbon-epoxy (0.5 mm)	Carbon-epoxy (0.5 mm)
Energy range (KEV)	40–3,000	50–3,000	6–3,000	3–3,000	6–3,000
Relative efficiency	22 %	29 %	40 %	34 %	40 %
Electronic chain					
HVPS	Inspector 2000 DSP Canberra	ORTEC	BERTAN	Inspector 2000 DSP Canberra	CANBERRA
Amplifier		DSPEC	ORTEC		CANBERRA
ADC		PLUS	SILENA		CANBERRA
Acquisition interface			SILENA		CANBERRA
Software					
Acquisition	GENIE 2000	GAMMAVISION	EMCA	GENIE 2000	GENIE 2000
Analysis		GESPECOR	GRILS (IAEA)		
Calibration procedure					
	Calibration with IAEA soil and water reference materials Efficiency transfer with LabSOCS	Soil standard RML traceability Efficiency transfer and coincidence summation correction with GESPECOR	Set of calibrated reference sources Efficiency transfer and coincidence-summing correction with PENELOPE	Detector characterization by Canberra (MCNP code) Efficiency transfer with LabSOCS Coincidence summing correction with Genie-2000	Detector calibrated using a sand standard of similar density prepared under the same conditions as the samples.
Counting time (s)	29,000	260,000	100,000	230,000	100,000

(MDA). For example, in the case of IFIN-HH, the underground μBq Laboratory, a few MDA values were: 1.6 Bq/kg (^{40}K), 0.24 Bq/kg (^{214}Pb) and 0.27 Bq/kg (^{214}Bi). For IFIN-HH, RML, the MDA values for the same radionuclides were: 4.1 Bq/kg (^{40}K), 0.90 Bq/kg (^{214}Pb) and 1.0 Bq/kg (^{214}Bi). Similar values characterize the CIEMAT measuring systems, with the exception of LMRI, whose measuring equipments were moved to a neighbor laboratory due to refurbishing of the radioactive installation and background levels were significantly higher. The background counting

rate was subtracted from the total absorption peak areas and its influence was accounted for in uncertainty budgets. Figure 2 presents a typical sample spectrum obtained at the IFIN-HH, underground laboratory.

Individual results and calculation mode

All participant laboratories calculated and reported the activities according to their procedures, taking into account the relations existing between the radionuclides in the natural series. Table 4 summarizes the results for all laboratories and reported activity concentrations, in Bq kg^{-1}, with their combined uncertainties, for a coverage factor $k = 1$. The components of the standard combined uncertainty were: net peak area, background subtraction, efficiency calibration of the system and software introduced uncertainties.

Discussion

Owing to the purpose of this work, that is the preparation of ^{226}Ra spiked slag, the activity of this radionuclide is the most important quantity; it also generates the important contributions in the gamma-ray spectrum, due to ^{214}Pb and ^{214}Bi; its value is directly influencing the uncertainty in

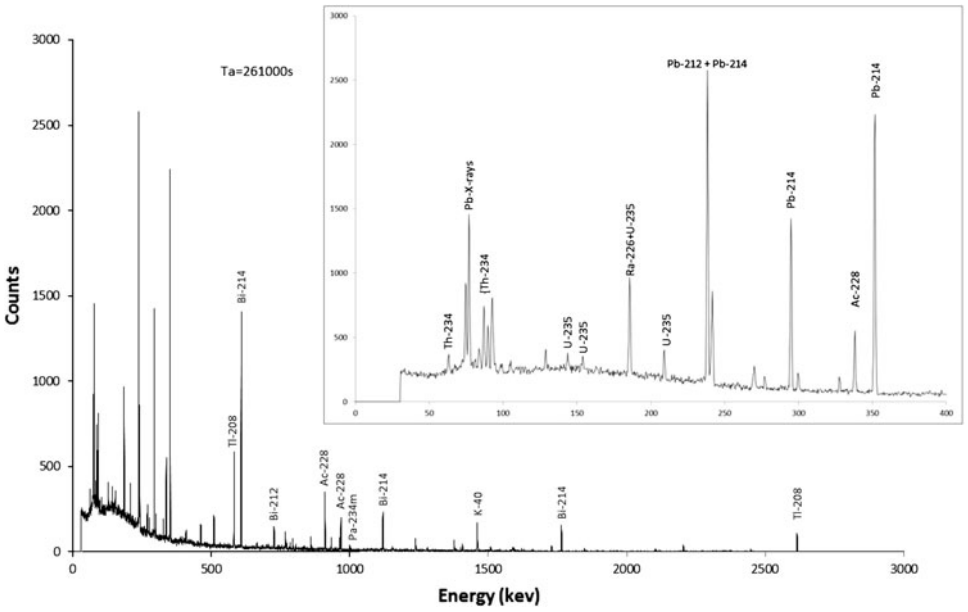

Fig. 2 HPGe spectrum of the slag sample, measurement in the underground laboratory

Table 4 Radionuclide activity concentration of the sample, in Bq kg^{-1}, reported by participants

Laboratory	IFIN-HH (μBq)	IFIN-HH, RML	CIEMAT, LMRI		CIEMAT, LMPR		CIEMAT, LRA
Radionuclide			Prompt	Equilibrium	Prompt	Equilibrium	Equilibrium
^{226}Ra	17.1 ± 2.7	14.0 ± 7.0	23.5 ± 14.3	18.9 ± 11.0	–	16.0 ± 9.0	13.8 ± 0.6
^{235}U	0.94 ± 0.14	1.13 ± 0.37	–	–	1.97 ± 0.9	1.5 ± 0.5	–
^{238}U	20.9 ± 0.4	25.0 ± 7.0	–	–	–	–	–
^{234}Th	–	26.4 ± 3.2	–	–	18.2 ± 3.3	22.0 ± 3.8	11.5 ± 2.8
^{234m}Pa	21.3 ± 3.0	26 ± 15	–	–	–	–	–
^{214}Pb	13.8 ± 0.4	14.3 ± 1.0	14.0 ± 1.7	16.0 ± 1.4	16.8 ± 1.5	17.5 ± 1.5	13.8 ± 0.6
^{214}Bi	13.1 ± 1.1	12.5 ± 0.8	13.2 ± 2.1	13.9 ± 1.7	15.3 ± 1.1	16.7 ± 1.1	13.9 ± 0.6
^{232}Th	8.22 ± 0.07	8.17 ± 0.23	–	–	–	–	–
^{212}Pb	8.15 ± 0.30	7.94 ± 0.38	9.5 ± 1.3	11.0 ± 1.0		12.0 ± 1.0	11.6 ± 0.8
^{212}Bi	8.47 ± 0.57	8.4 ± 1.3		9.2 ± 8.1		12.2 ± 1.3	9.8 ± 2.0
^{208}Tl	2.70 ± 0.13	2.27 ± 0.20	–	–	–	3.9 ± 0.3	–
^{228}Ac	8.29 ± 0.27	8.4 ± 0.8	–	–	–	10.2 ± 0.8	–
^{40}K	18.0 ± 1.1	16.8 ± 2.2	–	–		19.6 ± 1.9	29.6 ± 3.4

Table 5 Final data on activity concentration of the slag sample

Radionuclide	Arithmetic mean (Bq kg^{-1})	Weighted mean (Bq kg^{-1})	Median (Bq kg^{-1})
^{226}Ra	16.0 ± 1.0 (without value 23.5 from Table 4)	14.0 ± 0.6 consistent set (without value 23.5)	16.0 ± 9.0
^{235}U	1.38 ± 0.23	1.02 ± 0.13 consistent set	1.13 ± 0.37
^{238}U	22.95 ± 2.05	20.91 ± 0.40 consistent set	–
^{234}Th	22.2 ± 2.4 (without 11.5)	22.3 ± 2.5 consistent set (without 11.5)	22.0 ± 3.8 (without 11.5)
^{234m}Pa	23.6 ± 2.4	21.5 ± 2.9 consistent set	–
^{214}Pb	15.17 ± 0.59	14.20 ± 0.39 consistent set	14.3 ± 1.0
^{214}Bi	13.65 ± 0.39 (without 16.7)	13.62 ± 0.39 consistent set (without 16.7)	13.2 ± 2.1 (without 16.7)
^{232}Th	8.19 ± 0.03	8.22 ± 0.07 consistent set	–
^{212}Pb	10.0 ± 0.7	8.7 ± 0.6 discrepant set	9.5 ± 1.3
^{212}Bi	8.97 ± 0.33 (without 12.2)	8.55 ± 0.50 consistent set (without 12.2)	8.47 ± 0.57 (without 12.2)
^{208}Tl	2.96 ± 0.49	2.74 ± 0.38 discrepant set	2.70 ± 0.13
^{228}Ac	9.0 ± 0.6	8.48 ± 0.39 consistent set	8.4 ± 0.8
^{40}K	18.1 ± 0.8 (without 29.6)	18.1 ± 0.9 consistent set (without 29.6)	22.0 ± 3.8 (without 29.6)

activity of the ^{226}Ra spiked material. Both IFIN-HH laboratories measured the activity from the 186.21 keV FAP, corrected for the contribution of the 185.72 keV FAP from ^{235}U. At CIEMAT, LMRI measured also this FAP, applying the same ^{235}U correction. CIEMAT, LRA calculated ^{226}Ra activity from the measured ^{214}Pb value. All reported values agree within the reported uncertainties.^{235}U activity was measured from the 143.76 keV FAP area. The activities of ^{234}Th, ^{234m}Pa, ^{214}Pb, ^{214}Bi, ^{212}Pb, ^{212}Bi, ^{208}Tl, ^{228}Ac, ^{40}K were measured directly from the respective FAP areas, as usually is done. The direct measured values of individual laboratories agree within the reported uncertainties, except ^{40}K—LRA values. They are also in agreement with the decay chain equilibrium ratios [12], as follows. ^{226}Ra activity should be equal with that of its daughters: ^{214}Pb and ^{214}Bi at equilibrium. The values reported for prompt and secular equilibrium measurements are not statistically different, proving that in both cases the equilibrium is almost reached, as the recipients were sealed. The activities of ^{228}Ac and ^{212}Pb, should be approximately equal, within the uncertainties limits; the activity of ^{212}Bi should be 10 % higher than that of ^{212}Pb and the activity of ^{208}Tl should be 36 % from that of ^{212}Pb.

The activity of ^{238}U was calculated as a mean between the ^{234m}Pa measured value which, at equilibrium, is equal with that of mother, ^{238}U, and the calculation from the ratio of the natural uranium isotopes:

$$(a)_{^{238}U} = (a)_{^{235}U}/0.046 \quad (1)$$

The activity of ^{226}Ra can be different from that of ^{238}U, as Ra and U have a different chemical behavior. The activity of ^{232}Th was calculated as the mean of activities of ^{212}Pb and ^{228}Ac, in secular equilibrium with it.

Calculation of the mean activity concentrations

Three types of calculations were used: arithmetic mean, weighted mean and median values, to choose the recommended value to be used for the correction of the ^{226}Ra spiked activity and to calculate the final uncertainty value of the sample activity. The reported values used in calculation were chosen after applying the Chauvenet criterium for exclusion of discrepant data. Table 5 presents the calculated mean values for all reported radionuclides' activity concentrations. The clear outlier values, not considered for calculation of the means are indicated in parantheses. Two situations were more difficult to manage: in the case of ^{212}Pb the declared uncertainties were underestimated and in the case of ^{208}Tl only three values were available. In both situations all values were considered, although the sets were not consistent Taking into account the careful evaluation of uncertainties by the participants and the application of the Chauvenet criterion of exclusion, one may conclude that the weighted mean reflects best the combination of the individual results. Consequently, we recommend using the weighted mean activity concentration values to calculate the total activity of the sample and the activity due to the spiking with standard solution of ^{226}Ra.

Conclusions

- The methods used in five participant laboratories and the results obtained in the measurement of a slag sample are presented; the calculation of primordial radionuclides, ^{238}U and ^{232}Th, content is done.
- The individual results agree in most cases and also are in a good agreement with the natural decay chains relations.

– The weighted mean values, calculated after applying the Chauvenet exclusion criterion, are recommended as final values of the comparison reference values.

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