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Determination of ^{210}Pb by direct gamma-ray spectrometry, beta counting via ^{210}Bi and alpha-particle spectrometry via ^{210}Po in coal, slag and ash samples from thermal power plant

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Abstract In order to compare three different techniques and estimate radiological impact, activity concentration of ^{210}Pb in coal, slag and ash samples from thermal power plant "Nikola Tesla", Serbia, were measured, and results are presented in this study. Determination of ^{210}Pb was carried out in three ways: using HPGe gamma spectrometer and via in-growth of ^{210}Po and ^{210}Bi by alpha-particle spectrometry and proportional counting, respectively. The results obtained for three different techniques were compared. Statistical analysis and comparison of methods were carried out by combination of Z score and χ^2 statistical tests. Tests results, as well as values of measured activities concentrations obtained by alpha and gamma spectrometry, showed that gamma spectrometry is a valid alternative to time-consuming alpha spectrometry for low level activity measurements of ^{210}Pb. This remark is also valid even for gamma spectrometers with poor efficiency in low energy region.

Keywords ^{210}Pb · ^{210}Po · ^{210}Bi · Alpha-particle spectrometry · Gamma-ray spectrometry · Beta counting

Introduction

Coal plays an important role in electric power generation in many countries at the global scene and in Republic of Serbia as well. Thermal power plant "Nikola Tesla" (TPP NT) is a power plant complex, located on the river Sava, approximately 40 km from Belgrade. It is the largest one in Serbia, and its production covers majority of Serbia's needs for electricity. TPP NT uses lignite mined from the mining basin Kolubara as fuel—a total of 29.2 million tons in the year 2014 [1].

Coal, as the fossil fuel, contains numerous natural radionuclides from uranium and thorium decay chains. Uranium daughter products such as ^{210}Pb and ^{210}Po are very important due to their volatility properties during the combustion process. These radionuclides are partly released in the flue gases and can escape to the atmosphere, and considered to be main contributors to the internal radiation dose of humans [2, 3].

According to the International Atomic Energy Agency (IAEA), coal and products of its combustion (slag and ash) are labeled as naturally occurring radioactive material (NORM). The specific activities of natural radionuclides in the coal are in wide range and strongly depend on the geological formation of coal. Slag and ash, which have specific activities are up to 10 times higher, are often released into the environment causing an increase and/or redistribution of natural radionuclide content.

Majority of radionuclides in coal remains in the ash but some of the ash from coal-fired power plants escapes into the atmosphere. Pollutions from air could contaminate soil, water, vegetation, the whole ecosystem and human health in the vicinity of a coal fired thermal power plant [3].

Thus, the monitoring of the environment should be regularly performed in the vicinity of TPP, together with

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comprehensive analysis of radiological characteristics of coal, slug and ash samples in order to estimate the radiological risk for health of inhabitants.

Theory

^{210}Po and ^{210}Pb in the environment

Recent studies showed that the activity concentration of ^{210}Po and ^{210}Pb have increased in the environment as a result of human activities such as burning fossil fuels in thermal power plants, the industry of fertilizers, and by vehicles through exhaust fumes [4].

^{210}Pb is a natural radionuclide from uranium decay chain emitting beta and gamma radiation, with a relatively long half-life (22.3 years). It originates from lithogenic minerals in the subsoil [4].

^{210}Pb can be release into the environment from areas of sediment deposition, such as ash landfills from TPP. Once released in environment ^{210}Pb could find its way into ground water and can result in the contamination of drinking water.

The natural distribution of ^{210}Po in environment is mainly determined by its progenitor ^{210}Pb distribution. Also, it is influenced by possible exhalation of its gaseous precursor ^{222}Rn. Namely, if ^{222}Rn escapes from soil or rock matrix, ^{210}Pb is produced elsewhere, which leads to redistribution of this radionuclide and therefore to the temporarily disequilibrium between ^{210}Pb and ^{210}Po in the environment. Furthermore, ^{210}Pb usually is not in secular radioactive equilibrium with its precursors in uranium series in environmental samples [5].

^{210}Po is an alpha emitter with a relatively short half-life (138.4 days) and represents one of the most toxic substances due to its intense specific radioactivity, (1 μg of ^{210}Po has an activity of 1.66×10^8 Bq) [6]. ^{210}Pb is mainly accumulated in skeleton in human body while ^{210}Po accumulates in soft tissues such as muscles and the liver in organisms [4, 7]. After entering the human body a relatively rapid rise of ^{210}Pb daughter product ^{210}Po occurs. Consequently, ingestion/inhalation of ^{210}Pb leads to significant increase in internal exposure to radiation. Therefore, it is necessary to determine ^{210}Pb accurately in different environmental samples, which could be difficult due to its physical and chemical properties.

Methods for ^{210}Pb determination

Activity of ^{210}Pb can be determined by gamma—ray spectrometry via photo peak with relatively low emission probability, 4.252 %, at energy 46.639 keV. Coaxial HPGe (p-type) spectrometers, which are usually used in laboratories for routine measurements, generally have poor detection efficiency at lower energies. Thus, mentioned photo peak commonly have poor statistic, and is not well shaped, so the use of such spectrometers can lead to unreliable determination of ^{210}Pb activity concentration, especially for samples with low activity.

In order to obtain reliable and accurate results, in some cases radiochemical determination of ^{210}Pb activity is necessary. Specific activity of ^{210}Pb can be determined by measuring the beta activity of its daughter product ^{210}Bi ($E_{\beta\max} = 1.17$ MeV) or the alpha activity of its granddaughter ^{210}Po ($E_\alpha = 5.32$ MeV). In previously mentioned two methods, ^{210}Pb activity is determined by measurement of its progenies, and it is necessary to know the degree of equilibrium that exists between the progeny and its parent ^{210}Pb. For ^{210}Po a period of more than 4.5 months is required to reach 50 % and 18 months to reach 88 % in-growth. For ^{210}Bi, with half-life 5.01 days, 98 % of equilibrium is reached in 30 days [2]. Changes of relative activities for ^{210}Pb, ^{210}Bi and ^{210}Po in time in an isolated system are presented in Fig. 1.

Alpha spectroscopic measurement of the in-growth ^{210}Po can achieve an ultra low detection limit, often 100–1000 times lower than for gamma-ray spectrometry, and represents the most sensitive method for indirect determination of ^{210}Pb. For this kind of determination it is necessary to carry out a polonium extraction from the examined sample after a minimum 5 half-life periods (almost 2 years) from its collection. Two years period is very long, and certainly is not acceptable for routine measurements. Nevertheless, comparison could be performed after the shorter period of time, before the equilibrium is established, but in this case, in order to determine expected value of $A_{^{210}\mathrm{Po},\alpha}/A_{^{210}\mathrm{Pb},\gamma}*$ ratio, Bateman's equations should

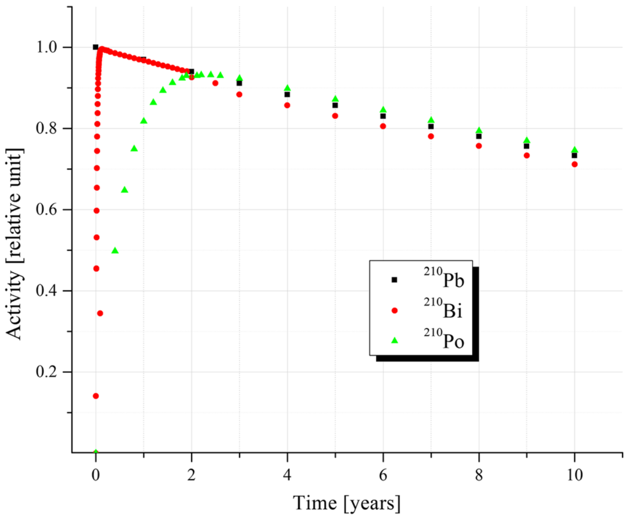

Fig. 1 Changes of relative activities for ^{210}Pb, ^{210}Bi and ^{210}Po in time in an isolated system

be applied. Regarding the quality control in testing laboratory such analysis should be performed in order to conduct internal comparison of results for ^{210}Pb activity obtained by gamma-ray spectrometry.

Since ^{210}Po is a pure alpha emitter, its determination can be carried out only by alpha-particle spectrometry. Passivated implanted planar silicon (PIPS) detectors are commonly used for that purpose. Spectroscopically thin alpha sources are usually prepared by spontaneous deposition of polonium ions onto less noble metal surfaces, such as nickel, copper or silver.

In case of ^{210}Pb determination through its daughter product ^{210}Bi flow-gas proportional counter is commonly used.

In this study, the activity concentration of ^{210}Pb were determined in coal, slag and fly ash samples (29 in total) originated from TPP NT by gamma-ray spectrometry and via in-growth of ^{210}Po and ^{210}Bi by alpha spectrometry and by beta counting, respectively.

Gamma-ray spectrometry measurement of ^{210}Pb was performed during the first half of 2013th, while alpha-particle spectrometry measurement of ^{210}Po was conducted in second half of August and first half of September 2015th. For 9 of these samples (three of each kind—coal, slag and ash) ^{210}Pb was determined by beta counting of in-growth ^{210}Bi in October 2015th.

Experiment

Sample collection and pre-treatment

For the purposes of this study, samples of analyzed coal, slag and ash (29 in total) were collected during the periodical emission tests in November and December 2011th at unit A1 of TPP "Nikola Tesla" and also in September 2012th at unit A3 of TPP "Nikola Tesla". Coal sampling was performed at feeders, before grinding process and drying coal in the mill. Slag was sampled during the transportation below the boiler, whereas ash was sampled in electrostatic precipitator pyramid hoppers, Fig. 2.

Coal, slag and ash samples were prepared for analysis (milled, dried, sieved and weighed) by appropriate standard methods, and ultimate and proximate coal analysis, proximate analysis of slag and ash were performed in accordance with ISO 17025.

Determination of ^{210}Pb by gamma-ray spectrometry

For gamma-ray measurement prepared samples of coal, slag and ash were placed in 125 ml PVC cylindrical boxes. The mass of the samples ranged from 64.85 to 97.99 g, depending on the sample density. All samples were measured by means of coaxial germanium semiconductor HPGe detector (ORTEC GEM-30, 37 % relative efficiency and 1.8 keV resolution for ^{60}Co at 1332 keV line). The detector was calibrated using the coal and soil matrix in identical cylindrical boxes spiked with common mixture of gamma-ray emitters (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr and ^{88}Y) certified by CMI (Czech Metrological Institute) [8]. Procedure of preparation of calibration standards is described in details in previously published paper [9], and efficiency curves used in this study have been verified through regular participation in interlaboratory comparisons and PT (proficiency test) schemes. In order to obtain valid curve, net peak areas of ^{60}Co and ^{88}Y were corrected for the coincidence summing effect applying the calculation method of Debertin and Schötzing [10]. The analytical expression of obtained efficiency curves was $\varepsilon = e^{-P(\ln E)}$, where ε is the detection efficiency, E is the energy and $P(\ln E)$ is the polynomial function of the fifth order. Uncertainty of the efficiency calibration includes uncertainty of radionuclides activities in standard, statistical uncertainty and uncertainty of efficiency curve fitting. Measurements of the prepared standards were performed in a close-to-detector geometry.

The obtained spectra were recorded using Canberra's Genie 2000 software. Recorded spectra were analyzed using Genie 2000, Aptec and Anges software, and all calculations were performed with the Mathematica 5.2 software (Wolfram Research Inc.). In order to achieve acceptable statistics, the samples were measured in a close-to-detector geometry from 66,000 to 250,000 s.

The activity concentrations of ^{210}Pb in coal, slag and ash samples were determined directly by analyzing full-energy peak at 46.54 keV.

Uncertainty of measurement results was determined by applying the general law of propagation of uncertainty. The largest contribution to the total uncertainty was due to the statistical uncertainty (up to 30 %) and efficiency calibration (5 %), whereas uncertainty due to measured mass of the sample and decay parameters could be neglected.

Determination of ^{210}Pb via in-growth of ^{210}Po by alpha-particle spectrometry

About 0.5 to 1 g of samples (coal, slag, and ash) was taken from PVC cylindrical boxes which was already used for gamma measurement and put into Teflon beaker. For recovery determination approximately 0.1, 0.2 and 0.3 g of ^{209}Po tracer was added into weighted coal, slag and ash samples, respectively. Specific activity of the tracer was (0.3373 ± 0.0064) Bq/g, on 01.07.2010. Further, beaker was placed onto plate on 200 °C for wet ashing. Wet ashing was carried out by adding 10 ml of concentrated HNO_3 and H_2O_2 in order to destroy organic matter. After

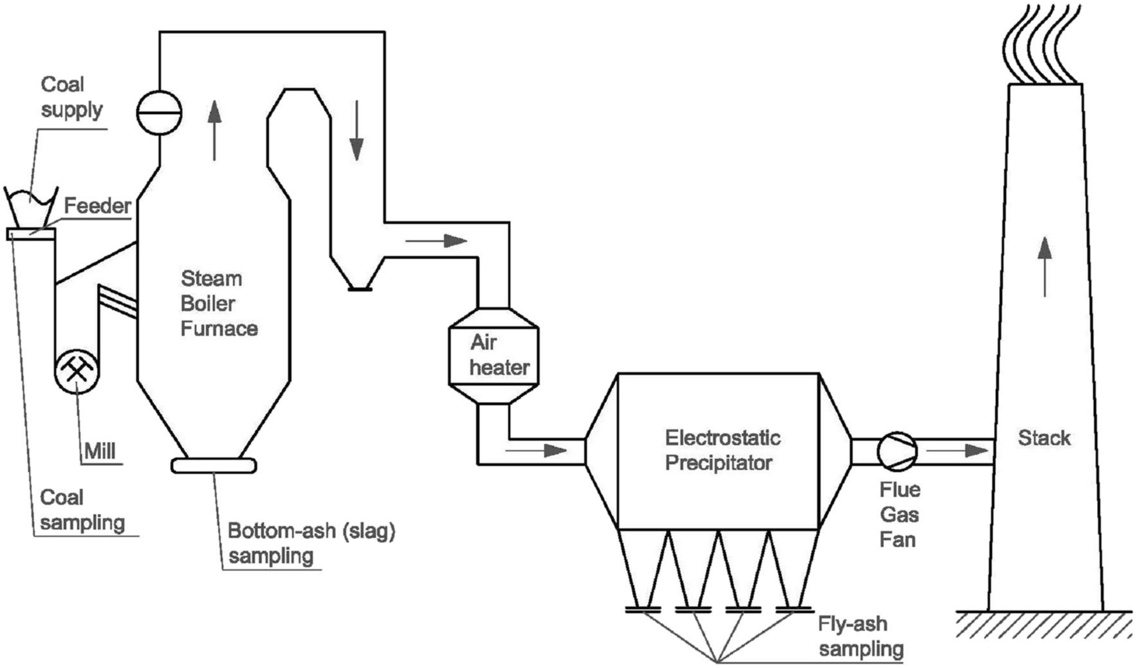

Fig. 2 Scheme of coal, slag and ash sampling places at TPP unit

evaporation to dryness, 10 ml of concentrated HNO_3, $HClO_4$ and HF were added successfully in that order, and left to evaporate to dryness. Dry residue was converted to chloride form with adding 5 ml of concentrated HCl and again evaporated to dryness. The dry residue was dissolved in 2 ml of concentrated HCl and diluted with distilled water to 100 ml volume. Then, 1 g of ascorbic acid was added into prepared solution in order to reduce iron ions (II and III) and eliminate interference from the silver disc during the deposition process [4]. The spontaneous deposition of polonium on a 19 mm diameter silver disk was carried out at 90 °C for 4 h. After the deposition was finished, the disk was rinsed with deionized water and dried on air. The disk was subsequently counted on alpha spectrometer described below, for activity determination and recovery calculation [2, 11].

For alpha spectrometric measurements of ^{209}Po and ^{210}Po an alpha spectrometer (Alpha Analyst, Canberra, USA), with passivated implanted planar silicon (PIPS) semiconductor detectors (active area of 450 mm^2 and efficiency of 28 % for diameter disk of 25 mm) was used. For calibration of the detector standard radionuclide source with following radionuclides: ^{238}U, ^{234}U, ^{239}Pu and ^{241}Am (code: 67978-121) was used. Standard radionuclides source was procured from Analytics, Inc. Data acquisition analysis was done in the Genie 2000 spectroscopy system software. Depending on the radionuclide activities in the samples the counting time varied from 1 to 7 days. Radiochemical recovery was determined by ^{209}Po activity measurement.

Determination of ^{210}Pb via in-growth of ^{210}Bi by proportional counting

In 9 out of 29 samples simultaneous determination of ^{210}Pb and ^{210}Po was performed in all three kinds of samples. At the beginning of the radiochemical procedure, besides ^{209}Po tracer, 25 mg Pb^{2+} of lead carrier were added to the samples. The dissolution of the samples was done as described in the previous chapter. The residue after total dissolution was dissolved in 2 M HCl and loaded on a Sr resin column (Eichrom Industries Inc.). The analytical method is based on selective separation of lead and polonium by extraction chromatography with bis-4,4′(5′)-t-butyl-cyclohexano-18,6-crown ether [12]. The non-retained ions were washed from the column with 2 M HCl. Polonium was stripped with 6 M HNO_3 while lead was removed with 6 M HCl solution. Obtained fractions were evaporated to dryness. Polonium source was prepared by self—deposition on a silver disk from HCl solution (pH = 1–2) with addition of 1 g of ascorbic acid to prevent deposition of interfering elements, as described in previous chapter. Polonium sources were measured by alpha-particle spectrometry.

Source for ^{210}Pb determination was prepared by precipitation of $PbSO_4$. Dry lead fraction residue was dissolved in water and concentrated H_2SO_4 was added. The precipitate was transferred to a counting planchet and its daughter radionuclide ^{210}Bi was measured at equilibrium on a low background gas flow proportional counter. For measurements a Canberra TENNELEC LB4100-W low background gas-flow proportional counter was used. Measurement system has eight proportional detectors in two drawers. Mixture of argon (90 %) and methane (10 %) was used as a counting gas. To allow corrections because of in-growth of ^{210}Bi and different self-absorption for samples with different radiochemical recovery measurement system was calibrated.

Results and discussion

^{210}Po and ^{210}Pb activities, measured by alpha-particle and gamma-ray spectrometry are presented in Table 1. Recovery was calculated through known quantity/activity of added tracer—^{209}Po, and ranged between 25 and 90 % while in the case of determination of ^{210}Pb by beta counting recovery was determined gravimetrically and varied between 35 and 64 %. From Table 1 it could be seen that results for ^{210}Pb specific activity obtained by semiconductor gamma spectrometry in 2013 are ranged from (16.5 to 116.0) Bq/kg, (20.1–60.8) Bq/kg and (84.3–153.0) Bq/kg, for coal, slag and ash, respectively. Obtained values were corrected for radioactive decay ($A_{^{210}\mathrm{Pb},\gamma}*$) to enable comparison of results.

Activities of ^{210}Pb measured by in-growth of ^{210}Po by alpha spectrometry in 2015 are also given in Table 1 and ranged from (11.9 to 160.5) Bq/kg, (21.1–49.7) Bq/kg, (75.6–151.0) Bq/kg for coal, slag and fly ash, respectively. The obtained values in the analyzed samples are in compliance with results obtained for specific activity of ^{210}Pb worldwide [13, 14]. The specific activities are the lowest in the coal samples, and the highest for the ash samples, as it was expected.

Table 1 Specific activities of ^{210}Po and ^{210}Pb, measured by alpha and gamma spectrometry, respectively

Sample label	Recovery (%)	$A_{^{210}\mathrm{Po},\alpha}$ (Bq/kg)	$A_{^{210}\mathrm{Pb},\gamma}$ (Bq/kg)	$A_{^{210}\mathrm{Pb},\gamma}*$ (Bq/kg)	$Z_{\gamma,\alpha}$ score	$A_{^{210}\mathrm{Po},\alpha}/A_{^{210}\mathrm{Pb},\gamma}*$
Coal-76	30.2	23.2 ± 1.5	27.8 ± 7.0	25.7 ± 6.5	0.374	0.9027
Coal-78	59.5	25.8 ± 1.0	30.4 ± 4.2	28.0 ± 3.9	0.546	0.9214
Coal-85	66.8	11.9 ± 0.6	16.5 ± 5.9	15.2 ± 5.4	0.607	0.7829
Coal-87	30.2	23.2 ± 1.2	26.1 ± 4.6	24.0 ± 4.3	0.179	0.9667
Coal-116	24.9	27.6 ± 1.8	31.8 ± 7.2	29.5 ± 6.7	0.274	0.9356
Coal-118	49.0	22.0 ± 1.0	22.7 ± 2.7	21.1 ± 2.5	−0.334	1.0427
Coal-141	43.7	41.8 ± 2.1	43.9 ± 4.7	40.8 ± 4.4	−0.205	1.0245
Coal-142	64.8	160.5 ± 7.9	116.0 ± 28.1	107.7 ± 26.1	−1.936	1.4903
Coal-143	42.0	21.9 ± 1.2	27.5 ± 6.2	25.5 ± 5.8	0.608	0.8588
Slag-82	37.7	35.0 ± 2.4	41.5 ± 7.3	38.3 ± 6.7	0.464	0.9138
Slag-83	72.2	35.4 ± 1.6	42.9 ± 12.4	39.5 ± 11.5	0.353	0.8962
Slag-84	63.5	35.4 ± 1.5	31.9 ± 7.5	29.4 ± 6.9	−0.850	1.2041
Slag-91	32.8	49.7 ± 2.7	60.8 ± 8.6	56.1 ± 7.9	0.767	0.8859
Slag-93	47.1	48.2 ± 2.1	54.3 ± 7.8	50.0 ± 7.2	0.240	0.9640
Slag-119	60.1	36.2 ± 2.0	42.1 ± 6.5	39.2 ± 6.1	0.467	0.9235
Slag-120	90.9	22.9 ± 1.0	28.9 ± 4.6	26.9 ± 4.3	0.906	0.8513
Slag-144	52.2	46.4 ± 3.9	52.9 ± 9.4	49.3 ± 8.8	0.301	0.9412
Slag-145	66.6	44.9 ± 1.7	45.7 ± 11.7	42.6 ± 10.9	−0.208	1.0540
Slag-146	66.0	21.1 ± 0.8	20.1 ± 3.0	18.7 ± 2.8	−0.824	1.1283
Ash-79	65.4	103.6 ± 4.7	101.1 ± 12.2	93.8 ± 11.3	−0.801	1.1045
Ash-80	52.0	94.5 ± 4.0	85.6 ± 10.2	79.3 ± 9.4	−1.488	1.1917
Ash-81	43.3	93.7 ± 3.7	88.3 ± 10.8	81.8 ± 10.0	−1.116	1.1455
Ash-88	32.4	80.7 ± 5.0	84.7 ± 6.8	78.6 ± 6.3	−0.261	1.0267
Ash-90	53.9	75.6 ± 2.9	84.3 ± 9.1	78.2 ± 8.4	0.293	0.9668
Ash-122a	42.7	151.0 ± 7.2	153.0 ± 17.7	142.7 ± 16.5	−0.461	1.0582
Ash-126a	61.4	128.6 ± 4.9	123.6 ± 11.8	115.2 ± 11.0	−1.113	1.1163
Ash-147	75.7	99.7 ± 3.8	91.7 ± 8.0	85.8 ± 7.5	−1.653	1.1620
Ash-148	54.3	89.6 ± 2.6	88.3 ± 7.4	82.5 ± 6.9	−0.963	1.0861
Ash-149	39.4	117.0 ± 4.4	114.5 ± 14.2	106.9 ± 13.2	−0.726	1.0945

Simultaneous representation of results obtained by alpha-particle spectrometry of ^{210}Po, gamma-ray spectrometry of ^{210}Pb and beta proportional counting of ^{210}Bi for nine samples are presented in Table 2.

Additionally, correlations between used techniques are presented in Figs. 3, 4 and 5. Strong correlation between alpha and gamma measurements could be noticed from Fig. 3 (adjusted $R^2 = 0.976$).

The highest discrepancy is for Coal-142 sample, but due to large number of samples/points, this does not affect good correlation.

On the other hand, correlations between gamma-ray measurements and beta counting is very weak (adjusted $R^2 = 0.361$) (Fig. 4).

Again, the highest discrepancy was obtained for sample Coal-142. Unlike the previous case, this point affects the correlation, but neglecting this value, correlation became much better (adjusted $R^2 = 0.868$) (Fig. 5), and somewise acceptable.

Reason for weaker correlation could be a smaller number of points compared to the correlation between gamma and alpha spectrometry and the fact that the beta counting measurement technique is less sensitive than alpha spectrometry. Also, should be taken into consideration that something is not right with sample Coal-142 (pre-treatment homogeneity etc.) and it should be examined.

Statistical analysis of the measurement results

In order to test statistical difference between two data sets—results of activity measurements performed for the same sample in two detector systems (alpha and gamma, gamma and beta), and to check if obtained results differed from the statistical point of view, Z score test was used for confidence interval of $\alpha = 5\ \%$ (Critical value $|Z_{0.05}| < 1.96$) [15].

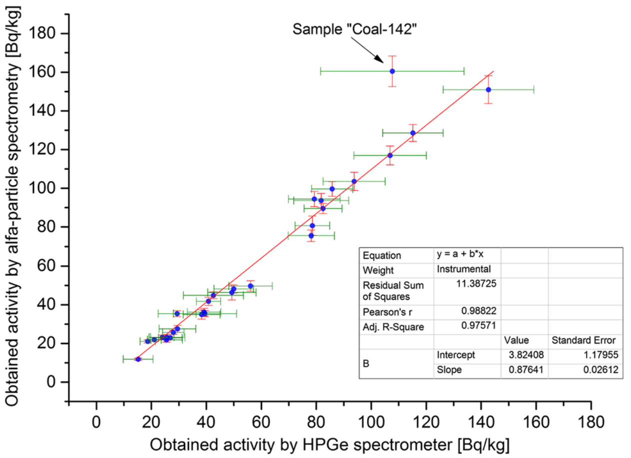

Fig. 3 Correlation between alpha-particle and gamma-ray spectrometry

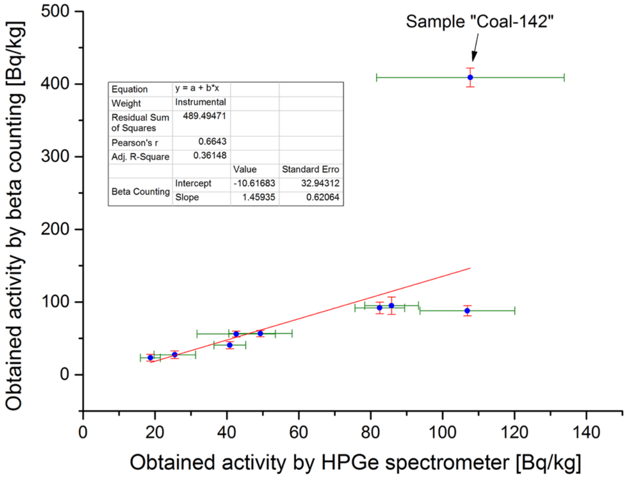

Fig. 4 Correlation between gas flow proportional counter and gamma-ray spectrometry

For all measured samples, results obtained by gamma and alpha spectrometry were not statistically different. For results of activity measurements obtained by gamma-ray

Table 2 Specific activities of ^{210}Po, ^{210}Pb and ^{210}Bi, measured by alpha and gamma spectrometry, and beta counting, respectively

Sample label	$A_{^{210}\mathrm{Pb},\gamma}*$ (Bq/kg)	$A_{^{210}\mathrm{Po},\alpha}$ (Bq/kg)	$A_{^{210}\mathrm{Bi},\beta}$ (Bq/kg)	$Z_{\gamma,\beta}$ score	$A_{^{210}\mathrm{Bi},\beta}/A_{^{210}\mathrm{Pb},\gamma}*$	$Z_{\gamma,\alpha}$–score	$A_{^{210}\mathrm{Po},\alpha}/A_{^{210}\mathrm{Pb},\gamma}*$
Coal-141	40.8 ± 4.4	41.8 ± 2.1	40.7 ± 5.0	0.015	0.9975	−0.205	1.0245
Coal-142	107.7 ± 26.1	160.5 ± 7.9	409 ± 13	−10.33	3.7976	−1.936	1.4903
Coal-143	25.5 ± 5.8	21.9 ± 1.2	27.5 ± 5.2	−0.257	1.0784	0.608	0.8588
Slag-144	49.3 ± 8.8	46.4 ± 3.9	56.7 ± 4.3	−0.756	1.1501	0.301	0.9412
Slag-145	42.6 ± 10.9	44.9 ± 1.7	56.0 ± 4.0	−1.154	1.3146	−0.208	1.0540
Slag-146	18.7 ± 2.8	21.1 ± 0.8	23.3 ± 4.7	−0.841	1.2460	−0.824	1.1283
Ash-147	85.8 ± 7.5	117.0 ± 4.4	95 ± 12	−0.650	1.1072	−1.653	1.1620
Ash-148	106.9 ± 13.2	89.6 ± 2.6	88 ± 7	1.265	0.8232	−0.963	1.0861
Ash-149	82.5 ± 6.9	99.7 ± 3.8	92.0 ± 8.0	−0.899	1.1152	−0.726	1.0945

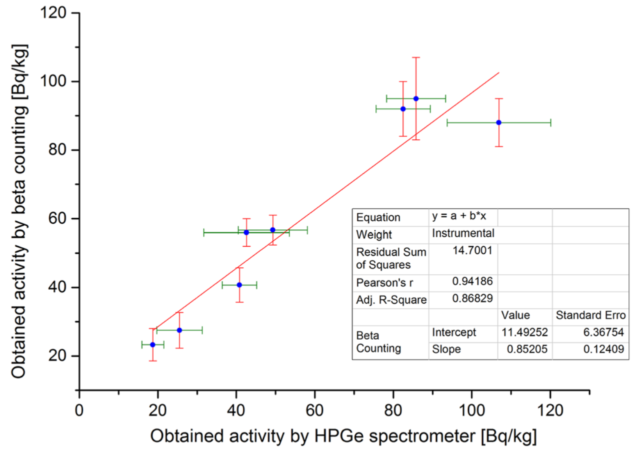

Fig. 5 Correlation between gas flow proportional counter and gamma-ray spectrometry neglecting value for sample Coal-142

spectrometry and gas flow proportional counter for 9 out of 29 samples *Z* score test showed that these results were not statistically different, except for sample Coal-142.

Also, to check the concordance of the two different methods used a simple test—combination of *Z* score and χ^2 tests—was used. For *Z* scores that are normally distributed the sum of the squared *Z* scores should follow a χ^2 distribution [16]. Thus, the next null hypothesis is:

H_0 There is no difference between two measurement techniques: alpha-particle and gamma-ray spectrometry for the determination of ^{210}Pb.

Starting from H_0 it was proved that (Z_i) (i = 1,…, n; where n corresponds to the number of degrees of freedom) are normally distributed. The significance level (type I—error) is set to $\alpha = 5$ % [17].

Accordingly, if alpha-particle and gamma-ray spectrometry differs by more than 5 %, H_0 should be rejected, otherwise, one can say that there is no statistical difference between the two techniques.

The results of the χ^2 test based on the $Z_{\gamma\alpha}$ score values for testing the H_0 hypothesis is presented in Table 3. It is statistically proved that two techniques are not significantly different at the confidence level of 5 % for the determination of ^{210}Pb.

For checking of the concordance between gamma spectrometry and gas flow proportional counting in this study, application of χ^2 test is not reliable due to insufficient number of measured samples.

Table 3 Statistical comparison based on the χ^2 test between alpha and gamma-spectrometry determination at the 5 % confidence level

γ parent	α emitter	Number of samples	χ^2	$\chi^2_{n,\alpha} = 0.05$	H_0 rejected
^{210}Pb	^{210}Po	29	17.16	41.34	No

Conclusion

In the present study three techniques (α and γ spectrometry, beta counting) for activity determination of ^{210}Pb are described and compared. The obtained results for three different techniques showed that in the most cases results are in good agreement, regardless their different sensitivity and they are within measurement uncertainties for all techniques used. A statistical comparison of results obtained by three different techniques was performed using *Z* score test. *Z* score values were lower than critical value for all compared results, except for one sample.

A statistical comparison of activities measured by alpha-particle spectrometry and gamma-ray spectrometry demonstrated that gamma spectrometry is a valid alternative to time-consuming alpha spectrometry for low level activity measurements.

Numerous factors can affect the reliability of the measurement results. Reliability of gamma spectrometry results is strongly affected by: poor detection efficiency at low energy region, background variation, performances of applied software for spectrum analysis, as well as difference in effective atomic number of measured sample and standard used for detector calibration. Different software packages differently calculate net area of the photo peaks and for poorly shaped peak could give different values for net peak areas and its uncertainty. Therefore, calculated radioactivity could be different. In this study, software Anges has proven to be the most reliable in terms of accurate determination of not-well defined net peak area. Difference between sample and calibration standard matrices is included in uncertainty budget through uncertainty of efficiency calibration.

On the other hand, alpha-particle spectrometry and beta counting are reliable, sensitive, and more suitable for samples with very low activity concentration but can be time consuming. Additionally, deposition time, applied temperature, type of backing material for cathode self-deposition disc and others, affect the quality of the source.

Besides above mentioned reasons, discrepancy between alpha-particle and gamma-ray measurement could be caused by the fact that, compared with sample mass for gamma spectrometry, very small quantity of the sample (~1 g) is used for alpha measurements. Small amount of the sample could be not representative for the hole bulk, due to possible presence of “hot-spots” in the bulk sample. This fact could be explanation for high value of discrepancies for sample Coal 142. For the same sample $Z_{\gamma\beta}$ score value was higher than critical one, which is in agreement with the assumption that sample Coal 142 is perhaps not homogeneous but it should be investigated.

For all these reasons determination of ^{210}Pb via in-growth of ^{210}Po by alpha spectrometry could be a very useful tool for gamma spectroscopy reliability testing. For a similar, statistically reliable conclusion regarding beta counting, it is necessary to perform measurements with a larger number of samples.

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