NUKLEONIKA 2024;69(2):93–97
doi: 10.2478/nuka-2024-0013

ORIGINAL PAPER

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Influence of the type of fuel used on the content of gamma radionuclides in the soot from the smoke ducts of the home furnaces

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Abstract. This paper presents the results of the measurements of gamma radioactive isotopes in soot samples from 15 different chimneys of household furnaces fired with various types of solid fuel. Soot samples were collected by the chimney sweep during the mandatory periodic cleaning of the chimneys. The γ-spectrometry technique using the high-purity germanium (HPGe) detector was employed for radiometry of the above-mentioned soot. It was found that the determined activity of gamma isotopes in soot is at a level similar to that in fly ash from power plants around the world. Artificial ^{137}Cs was detected only in the soot from the combustion of biofuel or mixed fuel. The results obtained were chemometrically analyzed to find the relationship between the fuel used and the gamma isotope content in the soot. The analysis of ^{137}Cs, ^{40}K, ^{228}Th, and ^{226}Ra is sufficient to differentiate between the soot obtained and tested, and it varied with the fuel type burned (fossil fuels/biofuels).

Keywords: Gamma isotopes • Household furnaces • PCA • Soot • TENORM

Introduction

Today, especially in the European Union, the use of fossil fuels to produce electricity and heat is gradually being abandoned. The use of ecological sources is preferred. However, for many years, the burning of various types of fuels in home boilers has been used for domestic hot water and to produce heat in winter for houses in rural areas. A gradual shift away from the typical fuel, which is coal, in favor of wood, wood pellets, and eco-peas has been observed. Unfortunately, there are still cases of burning waste and household garbage. The inevitable effects of burning any type of solid fuel are the formation of ash and soot, which can concentrate the radionuclides contained in the fuel. Materials with an increased content of natural radioactive isotopes called technologically enhanced naturally occurring radioactive material (TENORM) may pose a threat to the environment and people [1]. There are many works that describe the composition of the dust obtained from electrostatic precipitators and bag filters from industrial power plants [2, 3] and their impact on soil contamination in their vicinity [4, 5]. However, there are no studies describing the radionuclide content in soot. In this study, the aim was to take a detailed look at soot from home furnaces fired with various fuels. Home fireplaces do not have filters, so only soot testing allows conclusions to be drawn

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Received: 4 December 2023
Accepted: 26 February 2024

about substances emitted into the environment. This research was carried out to determine the content of gamma activity of natural radioisotopes: ^{226}Ra, ^{210}Pb (uranium series), ^{228}Th (thorium series), ^{40}K (primordial), and artificial ^{137}Cs in soot from smoke ducts of home furnaces. Also, an attempt was made to use chemometric analysis to distinguish between the radiometric compositions depending on the type of fuel used in the furnace.

Materials and methods

Soot samples from 15 different chimneys from home furnaces fired were collected by the chimney sweep during the mandatory periodic cleaning of chimneys. Samples were collected in the Lesser Poland Voivodeship (south Poland) in the rural municipality of Czernichów and Brzeźnica. On the basis of the testimonies given by the users, it was found that the fuels used were hard coal, eco-pea coal, wood pellets, various types of wood, and, in one case, plywood and chipboard. A detailed description with additional information is presented in Table 1.

Generally, the obtained soot did not require additional preparation; it was dry and very finely dusty, which allowed avoiding sieving. The exception was soot from chimney no. 7, (from chipboard and plywood), which resembled glassy stones. They were very hard and had to be broken with a hammer. All soot samples were brought to the same humidity by being kept in a dryer at a temperature of 50°C for at least 24 h. Then they were poured into identical cylindrical measuring vessels (made of transparent polystyrene) having a volume of 27 cm^3 and a diameter of approximately 4.9 cm. To maintain the identical measurement geometry, the vessels were always perfectly filled with the analyte (no empty spaces inside). The measuring vessels were then covered with parafilm (where the lid joined the base) to seal them so that radon gas could not escape from the vessel. This allowed within 3 weeks to achieve a radioactive equilibrium inside the vessel between ^{226}Ra and its decay products (e.g., ^{214}Pb and ^{214}Bi). Measurements were made using a gamma spectrometer with a high-purity germanium semiconductor detector (model Broad Energy BE3830 with a composite carbon window, by Canberra/Mirion, with a relative efficiency of 34%). The spectrometric amplifier, high-voltage power supply, memory buffer with analog-digital converter, and computer program (Genie-2000) were also produced by Canberra/Mirion. The spectrometer was equipped with low background shielding (from the inside – 0.1 cm Cu; 0.5 cm Cd; 5.5 cm low-activity Pb and 7.5 cm Pb). The low-activity lead used contained <6 Bq·kg^{-1} of ^{210}Pb. To determine the absolute efficiency (efficiency calibration), certified materials: IAEA-447, IAEA-RGU-1, and IAEA-RGTh-1 of the International Atomic Energy Agency were used. A more detailed description with the energy of the characteristic gamma-ray quantum, the methods used to calculate the measurement uncertainty, and the correction factors used are described elsewhere [6–9]. The following gamma radioisotopes were determined: artificial ^{137}Cs, natural ^{228}Th (from thorium series), ^{226}Ra, ^{210}Pb (from uranium–radium series), and ^{40}K. ^{228}Th was determined by its progeny: ^{212}Pb, ^{212}Bi, ^{208}Tl, whereas ^{226}Ra was by ^{214}Pb and ^{214}Bi. ^{40}K was measured by its spectrometric line of 1460.8 keV. This line may interfere with the line from ^{228}Ac (1459.1 keV). However, due to the fact that this spectrometric line (1459.1 keV) has a very low emission probability (0.87%) [10, 11] and there was few ^{228}Th in the tested samples (compared to the ^{40}K activity), this interference was not taken into account in the calculations.

Table 1. Detailed description of the fuels used on the basis of user testimony

Furnace no.	Description and additional information
1	Mixed wood
3	Coal + wood + carton
4	Eco-pea coal (in bulk)
5	Eco-pea coal (mine "Piast") + beech wood
7	Plywood and chipboard (shiny and extremely hard soot)
8	Coal (mine "Piast")
9	Hard firewood
10	Wood pellet (from "Zator")
12	Eco-pea coal (it created a lot of slag)
13	Eco-pea coal (bagged)
14	Eco-pea coal (mine "Piast Ruch 2")
15	Eco-pea coal
17	Construction timber + firewood hardwood
20	Beech + aspen wood
22	Mixed wood + cardboard

Results and their statistical analysis

Table 2 presents the obtained results of the gamma measurements and the density of individual samples. Table 3 shows the basic statistical parameters of the obtained results and the minimum detectable activity (MDA) values (the lower limit of detection (LLD) values are three times lower than the MDA).

The results show that both natural radionuclides and artificial ^{137}C are present in the soot from home furnaces. Since no results from other studies on home furnace soot were found, the results obtained can only be compared with the radionuclide content in fly ash and slug. In fly ash from power plants, the average activity for ^{226}Ra was in range of 546–1288 Bq·kg^{-1}, for ^{40}K: 413–642 Bq·kg^{-1}, and ^{210}Pb: 396–3335 Bq·kg^{-1} [2]. In other works, it was found in fly ash: ^{226}Ra: 10.5–136 Bq·kg^{-1} (for biomass combustion), ^{228}Ra (if radioactive equilibrium with ^{228}Th is assumed): 5.2–78.2 Bq·kg^{-1}, and ^{40}K: 419–1466 Bq·kg^{-1} [3]. In the ash from home furnace activity, ^{226}Ra, it was in the range 112–163 Bq·kg^{-1}, ^{228}Ra (^{228}Th): 71.4–100 Bq·kg^{-1}, and ^{40}K: 211–857 Bq·kg^{-1} [3]. Comparison of the results for artificial ^{137}Cs is difficult due to its relatively short half-life (30 years) and dispersion in the environment, but its high content was observed in the ash after burning

Table 2. Results of the spectrometric measurements with uncertainty

No.	Density ($G \cdot cm^{-3}$)	^{137}Cs ($Bq \cdot kg^{-1}$)	^{40}K ($Bq \cdot kg^{-1}$)	^{228}Th ($Bq \cdot kg^{-1}$)	^{226}Ra ($Bq \cdot kg^{-1}$)	^{210}Pb ($Bq \cdot kg^{-1}$)
1	0.53	14.33 ± 0.52	671 ± 24	MDA	15.6 ± 2.6	411.9 ± 5.8
3	0.30	5.12 ± 0.76	323 ± 39	15.8 ± 7.5	17.9 ± 4.6	467.3 ± 9.5
4	1.32	MDA	LLD	MDA	15.2 ± 1.6	111.0 ± 15.0
5	0.40	16.30 ± 1.10	LLD	30.6 ± 9.3	35.6 ± 4.7	395.0 ± 44.0
7	0.76	MDA	MDA	MDA	MDA	52.0 ± 16.0
8	0.30	3.42 ± 0.68	72 ± 35	17.4 ± 9.8	26.8 ± 4.5	376.6 ± 8.3
9	0.54	18.75 ± 0.59	180 ± 22	MDA	MDA	225.7 ± 5.3
10	0.48	68.12 ± 0.96	400 ± 26	20.9 ± 6.5	30.4 ± 3.1	649.9 ± 7.7
12	0.68	MDA	122 ± 17	36.5 ± 6.0	32.8 ± 2.3	1098.7 ± 7.3
13	0.16	MDA	MDA	36.0 ± 19.0	74.1 ± 8.9	663.0 ± 16.0
14	0.48	LLD	LLD	47.5 ± 8.6	83.9 ± 3.3	576.0 ± 7.4
15	0.47	MDA	93 ± 22	41.3 ± 8.1	61.9 ± 3.1	392.5 ± 5.8
17	0.56	28.86 ± 0.64	650 ± 24	10.9 ± 8.5	12.6 ± 2.6	402.0 ± 6.0
20	0.48	22.50 ± 0.56	372 ± 23	15.6 ± 6.2	26.9 ± 2.9	248.6 ± 5.1
22	0.48	17.17 ± 0.64	797 ± 28	11.2 ± 7.9	14.8 ± 3.0	428.2 ± 6.9

LLD, lower limit of detection; MDA, minimum detectable activity.

Table 3. Basic statistical parameters of the obtained results and the value of minimum detectable activity (MDA)

	Minimum	Maximum	Average	Standard deviation
Density ($g \cdot cm^{-3}$)	0.16	1.32	0.53	0.11
^{137}Cs ($Bq \cdot kg^{-1}$)	MDA (<1.5)	68.1	13.6	1.6
^{40}K ($Bq \cdot kg^{-1}$)	MDA (<23.7)	796.7	260.6	103
^{228}Th ($Bq \cdot kg^{-1}$)	MDA (<0.88)	47.5	20.2	9.5
^{226}Ra ($Bq \cdot kg^{-1}$)	MDA (<1.3)	83.9	30.7	6.9
^{210}Pb ($Bq \cdot kg^{-1}$)	MDA (<5.4)	1098.7	433.2	6.4

Table 4. Eigenvalues and percentage of the variance described in principal component analysis

Component no.	Eigenvalue	Percent of variance	Cumulative percentage
1	2.79	46.58	46.58
2	1.61	26.96	73.54
3	0.66	11.11	84.65
4	0.53	8.91	93.56
5	0.32	5.40	98.97
6	0.06	1.02	100.00

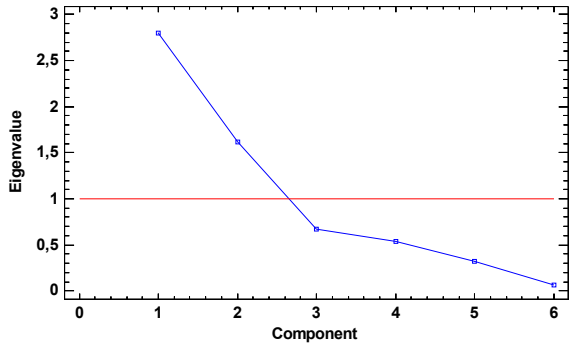

Fig. 1. Principal component analysis scree plot.

the biomass [12]. Generally, it can be assumed that for various fuels, the results obtained for soot are in the same range as those for fly ash.

Further interpretation of all the obtained results is quite difficult due to their high variability; therefore, principal component analysis (PCA) was used. Detailed applications of PCA in the analysis of other radiometric results have been described elsewhere [13–16]. PCA was done in the Statgraphics Centurion 18 computer program. Since the absence of a numerical value (such as MDA or LLD) is not allowed in the statistical analyses, for the current PCA analysis, the MDA values were set as half of the MDA values in Table 3 and the LLD values were set as half of the LLD values. The PCA was conducted for 15 cases studied and 6 variables (an additional variable was the density of the soot). After standardization, two principal components were extracted (of the six possible), because only they had eigenvalues greater than one. Table 4 shows the parameters of the PCA analysis conducted. The cumulative eigenvalue of the first two principal components was 4.4, and they explain 73.5% of the observed variance. The scree diagram (Fig. 1) also indicates that, for further interpretation, it is enough to separate only the first two principal components.

The PCA biplot (Fig. 2) carried out on the obtained results allowed an almost perfect division of the tested soot due to the combusted fuel from which they were produced.

In this diagram, changes in the concentrations of the individual radionuclides were observed in the space of the first two principal components. It can be seen that the activity of ^{226}Ra and ^{228}Th increases for burned fossil fuels (additionally, it can be seen that these activities are very well correlated). At the same time, the content of ^{40}K and ^{137}Cs increases for the soot produced by the combustion of organic fuels (it can be seen that these activities are also cor-

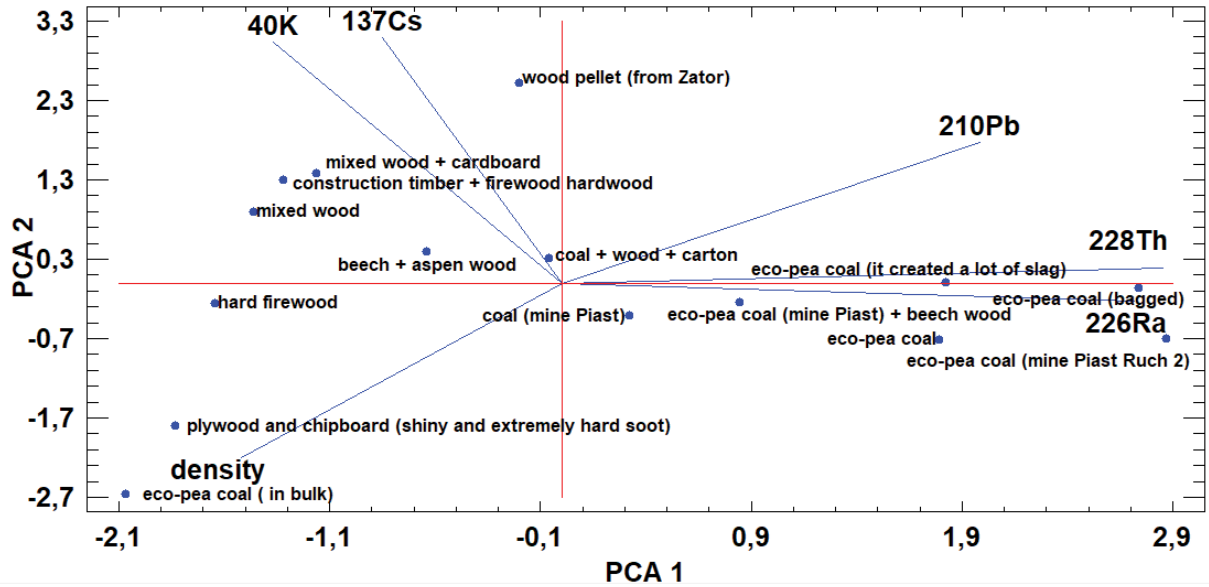

Fig. 2. Principal component analysis of the measurements results.

related but lower than that of ^{226}Ra and ^{228}Th). The soot resulting from the combustion of mixed fuels is located in the center of the biplot, and its location may probably indicate the ratio in which these fuels were mixed. It seems that the activity of ^{210}Pb does not differentiate the tested samples; however, it can be noticed that the activity of ^{210}Pb and density are negatively correlated.

The two samples with high soot density (bottom left of the graph) should be taken into account: first is the soot from chimney no. 7 (glassy stones with a density after breaking of 0.76 g·cm^{-3}). This hardness and glassiness probably resulted from the presence of unburnt glue, which is the main ingredient in this fuel. The second is the soot from furnace no. 4 where its density reached 1.32 g·cm^{-3} (the average for other soot was 0.47 g·cm^{-3}). This soot is the result of the eco-pea coal (bulk) combustion. There is no good explanation for why it has such a high density. There are three possible causes for this condition:

- bulk eco-pea coal was burned – hence, it could have had a high moisture content and did not burn completely,
- bulk eco-pea could contain a large amount of nonflammable impurities, and
- furnace malfunction or incorrect service by the owner resulted in incomplete combustion of the coal.

Without additional research, it is not possible to determine the cause of this condition because the very low activities of all the tested isotopes may be the result of any of the three hypothetical causes.

Conclusions

Soot from home furnaces contains TENORM and artificial ^{137}Cs at levels similar to those in fly ash from power plants. It can pose a health hazard, especially for chimney sweepers who are in close and frequent contact with it during their work.

Performing PCA makes it easier to interpret the results obtained. PCA analysis allowed us to determine that:

- radioactivity of ^{210}Pb (in soot) does not differentiate between fuels burned,
- a high content of ^{40}K and artificial ^{137}Cs indicates the use of biofuels, while a high content of ^{226}Ra and ^{228}Th indicates the combustion of fossil fuels,
- it is possible to determine an approximate ratio of organic to fossil fuel (based on the position on the biplot) if a mixed fuel is used,
- in the soot from the smoke ducts of the home furnaces, activities of ^{226}Ra and ^{228}Th are well correlated and ^{137}Cs and ^{40}K are also correlated but to a lesser extent, and
- density and activity of ^{210}Pb are negatively correlated in soot.

Acknowledgments. This work was partially supported by the research subvention supported by the Polish Ministry of Education and Science grant no. 16.16.210.476. Special thanks to the student from AGH, Miss Aleksandra Zabagło, for her help in obtaining and preparing samples.

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