Determination of ^{210}Po in air filters from metallurgic industry

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Abstract

The elevated concentration of ^{210}Po attached to aerosol particles inside a non-ferrous metal refinery was studied. The aerosols were collected on Petrianov or glass-fiber filters and subsequently subjected to radiochemical procedure consisting of acid leaching and concentration by micro co-precipitation with manganese oxide. For the activity determination alpha spectrometry and liquid scintillation counting (LSC) were applied. The obtained results showed that usually observed polonium concentration inside the plant was lower than 78 mBq m^{-3} , however short spikes up to $7430 \pm 710 \text{ mBq m}^{-3}$ (related to the specific thermal process) were also observed.

Keywords Polonium in air · Polonium by LSC · TENORM in industry · Polonium contamination

Introduction

The presence of some radioactive elements in the environment is strictly connected with the term NORM (Naturally Occurring Radioactive Materials), which refers to all materials (e.g. rocks, minerals, soil) containing radionuclides. The presence of NORM materials is natural, and therefore is rarely a concern from radiation protection point of view. On the other hand, processing of some NORM materials leads to production of so called TENORM (Technologically Enhanced Naturally Occurring Radioactive Materials). This term encompass any material in which concentration of NORM was increased, and therefore can pose a radiation hazard to humans [1]. The main sources of TENORM are found in some sectors of heavy industry like mining, coal combustion, metal ores processing, phosphoric acid and phosphate fertilizers productions [2, 3].

^{210}Po is a part of ^{238}U decay chain, which is the main component of TENORM radioactivity. Concentration of ^{210}Po in urban air in Poland is reported to be ranging from 0.01 up to 0.431 mBq m^{-3} [4]. The element is known for its high toxicity and radiotoxicity.

In industrial processes polonium, if present, tend to escape from the material during high temperature processing due to high volatility. Therefore it is rarely a concern for radiation protection of personel. On the other hand polonium is usually removed by gas flux into the exhaust stack, where attached to the particulate matter can: adsorb on the venting system walls, be captured by exhaust gases purification system or be released to the atmosphere, what may be a concern from the environmental protection point of view [5].

Lack of studies on this issue still remains. Only one known case is well described, namely radioactive contamination in the vicinity of Capper Pass Ltd. tin smelter in Melton (United Kingdom). In this case processing of uranium bearing minerals caused a release of ^{210}Po enriched dust into the atmosphere. The observed off-site concentrations of ^{210}Po in air ranged from 0.007 to 0.56 mBq m^{-3} , while background values were to be $0.0023\text{--}0.26 \text{ mBq m}^{-3}$. What is more, the on-site concentrations of polonium were as high as 2.4 mBq m^{-3} [6].

This study focused on developing of the analytical methods for ^{210}Po determination in air filter as a part of radiological risk assessment in non-ferrous metal refinery.

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Experimental

Sampling

The aerosol samples were collected in two sections of a non-ferrous metals refinery, in western Poland, where ^{210}Po containing waste materials from electrorefining are reprocessed. The first set of samples was collected in hydrometallurgy section, where post electrorefining sludge is subjected to acid leaching and selective reduction. The second set of samples was collected in molding section, where product from hydrometallurgy (noble metals concentrate) is purified and casted into bars.

The aerosol samples were collected using High Volume Air Sampler type DFHV-1DT (F&J Speciality Products inc., USA) equipped with two types of sampling heads. A standard sampling head with dedicated glass fiber filters (50 mm in diameter) was used in hydrometallurgy section. The sampler was mounted in the middle of the hall, where air is intensively mixed by the mechanical ventilation and therefore considered homogeneous.

In the molding section high instability of air composition was observed (e.g. local dust emissions). In order to obtain relevant results for dose calculation, sampling head on the extension hose was developed. The head was equipped with Petrianov filters (50 mm in diameter) attached to the 3 m extension hose. During sampling, the head was kept near the furnace operator's face in order to collect representative samples of breathed air.

In total, eight filters were sampled. Two of the filters (#1 and #3) were sampled from the hydrometallurgy section. Filter #1 was sampled in the beginning of the day shift (startup of the installation). Filter #3 was collected during normal operation of the installation. The remaining samples were collected from the molding section. Samples #2 and #4 were collected during loading of a furnace, sample #5 during melting of the feed, and sample #6 covered the entire molding process. Sample #7 was collected during loading and melting, while sample #8 was sampled during casting procedure.

Preliminary alpha measurements

The obtained filters were preliminary measured with RUM-2 radiometer (Polon Alfa, Poland) coupled with ZnS/organic glass solid scintillation probe SSA 1-P (Polon Alfa, Poland). Filters were measured for 600 s in total alpha counting mode. The set was calibrated by use of surface ^{241}Am source. Detailed sample list and results of the total alpha activity are presented in Table 1.

Table 1 The total alpha activity measured during initial screening of filter samples

Sample	Sampling period (min)	Air volume (m^3)	Total alpha radioactivity (Bq)	Activity concentration (Bq m^{-3})
#1	60	6.00	0.35 ± 0.05	0.058 ± 0.008
#2	10	9.24	0.17 ± 0.02	0.018 ± 0.002
#3	40	4.00	0.22 ± 0.03	0.055 ± 0.007
#4	5	0.52	0.18 ± 0.03	0.35 ± 0.06
#5	20	2.00	0.12 ± 0.02	0.06 ± 0.01
#6	39	3.90	4.38 ± 0.66	1.1 ± 0.2
#7	34	4.50	1.17 ± 0.18	0.26 ± 0.04
#8	3	0.45	2.45 ± 0.37	5.4 ± 0.8

Table 2 Microwave digestion conditions

Step	Duration (min)	Minimum pressure (bar)	Maximum pressure (bar)	Maximum temperature ($^{\circ}\text{C}$)
1	5	18	20	250
2	15	35	39	270
3	20	39	43	270

Polonium extraction

In order to develop the most efficient method of extraction of polonium from the sample, single filter (glass fiber) was cut into 25 smaller (5 mm diameter) discs. First 5 discs (from different regions of the filter) were mixed together and spiked with ^{209}Po tracer solution. The sample was decomposed in microwave digestion system. The system was equipped with closed PTFE vessel preventing polonium vapors from escape. Parameters of the digestion program are described in Table 2.

This technique provided the complete dissolution of a sample, thus yield of polonium extraction was considered as 100%. The microwave digestion was suitable only for glass fiber filters. In case of Petrianov filters it was not possible to achieve total dissolution, carbonized residue attached to the vessel wall was found in every experiment.

The sample from the microwave digestion system was considered as reference sample for calculation of the acid leaching techniques yield. In total 5 different leaching agents were studied. Firstly, diluted oxidizing and non-oxidizing acids, as described by Bem and Komosa [7–9], were tested. For each experiment 5 discs were mixed together. In order to control the radiochemical procedure the samples were spiked with ^{209}Po tracer solution. Due to unsatisfactory performance of the leaching, more concentrated acids and *aqua regia* were tested. All leaching

experiments were performed in ambient temperature, in closed vessels. Results are shown in Table 3.

Alpha measurements

The radiochemical procedure for alpha measurements comprised of acid leaching, co-precipitation with manganese oxide, chemical decomposition of the precipitate and spontaneous deposition on silver plates. Each sample was leached with 12 mL of *aqua regia* in 50 mL Erlenmeyer's flask for 48 h. Samples were previously spiked with ^{209}Po tracer solution. The obtained solution was filtered in order to separate the solid residue. The solution was transferred into glass beaker and diluted with 38 mL of deionized water. Polonium was pre-concentrated by co-precipitation with manganese oxide. Sample was alkalized to pH=9 by the use of 25% ammonia solution. Afterwards 2 mL of 0.2 M MnCl_2 and 2 mL of 0.3 M KMnO_4 were dropped while intensive stirring. The obtained precipitate was centrifuged and dissolved in 10 mL of 25% hydroxylamine solution in 0.5 M HCl. After dissolution of the precipitate, the samples were transferred into PTFE deposition vessel. Polonium was plated on silver discs (25 mm diameter) mounted to the bottom of the vessel. The plating was carried out at 85 °C for 4 h. The alpha sources were left for 48 h before measurement for short-lived polonium isotopes to decay. The measurement was performed in Alpha Analyst (Canberra) spectrometer equipped with 450 mm² PIPS detectors. The activity calculation were corrected for the decay of ^{210}Po during storage and measurement of the sources.

Liquid scintillation counting

It was estimated that samples are unsuitable for alpha spectrometry if preliminary measurements gave results greater than 1 Bq of total alpha radiation. Performing analyses of these samples would have required the use of proportional amount of tracer solution or diluting an extract. These methods were found unsatisfactory from the practical point of view. In order to analyze these samples a radiochemical procedure for liquid scintillation counting (LSC) was

developed. This method was chosen as it allows to analyze samples of activity greater than 1 Bq, and does not require high amounts of tracer solutions. The procedure comprised of acid leaching, co-precipitation with manganese oxide, chemical decomposition of the precipitate and separation by liquid–liquid extraction. The first two steps were similar as described in the alpha procedure, however no tracer solution was used. The obtained precipitate was decomposed in 5 mL of 40% hydroxylamine in 0.5 M HCl solution, and the sample was transferred into separating funnel with addition of 10 mL of 2 M HCl. Polonium was extracted twice with 5 mL of 0.5 M solution of *tri*-octylphosphine (TOPO) in toluene. After the extraction, the organic phase contained 100% of ^{210}Po and ^{210}Bi , while ^{210}Pb remained in the aqueous phase, as described by Bem [6]. For the analysis 9 mL of the organic phase was transferred into a 20 mL plastic vial and mixed with 11 mL of scintillation cocktail Ultima Gold AB (Canberra). The samples were counted in Tri-Carb liquid scintillation counter type PE 3180 TR/SL (PerkinElmer) for 10,000 s in fixed channel mode. The energy calibration for polonium was performed with pure ^{209}Po solution.

The combined chemical recovery and counting efficiency for this method was calculated on the basis of 3 samples of known ^{210}Po activity.

Results and discussion

Leaching yields

The obtained results are shown in Table 3 reveals that 48 h of leaching with *aqua regia* is the most beneficial for analyzed filters.

The most important disadvantage of this method is the long time of leaching, which is however compensated by high yield, low work consumption and insensibility to filter type. This method was selected also because, unlike microwave digestion, it allowed to digest the entire sample in one operation.

The chemical yields of leaching were different than reported by other researchers. Strongly oxidizing digestive

Table 3 Yield of polonium extraction from air filters by various leaching

Extraction method	Destructive agent	Total volume of reagents (mL)	Time (min)	Yield (%)
Microwave digestion with <i>aqua regia</i>	$\text{HNO}_3 + \text{HCl}$	6	30	100 ± 11
Diluted non-oxidizing acid leaching 1	2M HCl	100	45	17 ± 3
Diluted oxidizing acid leaching 2	2M HNO_3	100	45	45 ± 6
Concentrated non-oxidizing acid leaching 1	6M HCl	100	120	68 ± 8
Concentrated oxidizing acid leaching 2	6M HNO_3	100	120	73 ± 7
<i>Aqua regia</i> leaching	$\text{HNO}_3 + \text{HCl}$	12	2880	97 ± 7

agents gave better yields than non-oxidizing [10]. Possible explanation is that it is the effect of specific (containing high amount of noble metals) matrix composition where polonium is bonded more by chemisorption than physical adsorption, as described by Kirby [10].

Polonium in air filters

The obtained alpha spectra were characterized by good resolution, since the FWHM for ^{210}Po was 21 keV. The chemical yield of the radiochemical procedure was in the range of $55 \pm 3\%$ to $87 \pm 4\%$, which after taking into account leaching yields gave 53 ± 4 – $84 \pm 7\%$ of total polonium transfer from the filter to the source. In LSC procedure the combined chemical yield and counting efficiency was $90 \pm 8\%$. A typical LSC spectra of a sample is presented in Fig. 1.

Re-counting of the vials after 4 months allowed to verify that no parent isotopes were present in the samples.

The obtained results of ^{210}Po activity are presented in Table 4 polonium concentration was calculated by dividing the inventory by the volume of sampled air.

Five samples (#1, #3, #4, #5, #6) were in good agreement with the preliminary results. Two samples (#7, #8) were characterized by lower ^{210}Po content than total alpha activity, in one sample (#2) ^{210}Po concentration was significantly higher than predicted. It may be the effect of large amount of dust collected on the filter or its unstable composition. It is worth noting that preliminary results were used as indicator to select proper method of the analysis and therefore no accuracy improvements in this method were implemented.

Table 4 ^{210}Po activity and concentration in air inside the plant

Sample	^{210}Po activity (Bq)	^{210}Po concentration in air (mBq m^{-3})
#1	0.30 ± 0.04	65 ± 8
#2	2.2 ± 0.6	240 ± 70
#3	0.25 ± 0.02	78 ± 8
#4	0.20 ± 0.02	382 ± 26
#5	0.10 ± 0.01	49 ± 6
#6	4.27 ± 0.64	1300 ± 200
#7	0.7 ± 0.1	200 ± 30
#8	1.7 ± 0.3	4730 ± 710

Among the final results three groups can be distinguished. For better illustration the results are arranged in ascending order and shown in Fig. 2.

Group L: Filter number 1, 3 and 5 were characterized by the lowest observed activity, lower than 78 mBq m^{-3} . These filters contained particulate matter collected from both of the sections, during normal operations with closed apparatus doors. As mentioned before, all of the apparatus were equipped with individual venting system. The system was efficient enough to create partial vacuum inside reaction chambers, thus no polonium vapors were released outside.

Group M: The filters number 2, 4 and 7 were sampled during loading of the furnaces in the molding section. The elevated level of radioactivity (240 – 1300 mBq m^{-3}) was observed due to partial escape of the smoke/dust during loading with the open door of the furnace.

Fig. 1 Typical LSC spectra of polonium extracted from air filter

Fig. 2 ^{210}Po concentration in air in ascending order

Group H: The highest activity of ^{210}Po was observed for filters #6 and #8. Both of the filters were collected during the casting procedure. In this case possible explanation was found. In order to prevent the liquid metal to adhere to the mold's wall, prior to casting it is heated in gas flame and intentionally covered with soot. While molten metal is poured into the mold heat causes the soot to burn, and therefore create high amount of dust in the air. Airborne dust acts like a carrier for polonium.

Conclusions

A method for polonium determination in particulate matter generated during waste materials reprocessing was developed. The initial step of acid leaching with *aqua regia* was essential for removal of polonium from metals—containing matrix. The radiochemical separation followed by alpha particles counting was suitable for samples of total activity lower than 1 Bq. For more active samples liquid–liquid extraction and LSC method was introduced.

The observed ^{210}Po concentrations in air in studied plant varied widely, however for most of the time concentration observed did not exceed 100 mBq m^{-3} . The highest concentrations were observed during high temperature

processes carried out outside the apparatus. It is worth mentioning that the concentration of polonium in air decreases significantly instantly with the end of process. What is important from the radiation protection point of view during this process is that the operator is obligated to wear gas mask with charcoal filters, which reduces the amount of inhaled ^{210}Po . While operating with closed doors the venting system occurred to be efficient enough to prevent polonium from escaping into the hall.

Upon results and further analysis of urine samples collected from the workers of the refinery, precise dose calculation will be performed. However preliminary results basing on the ICRP recommendation for dose calculation via inhalation were made. The observed concentrations however elevated, remain on safe levels [11].

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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