Determination of radioactivity in air filters by alpha and gamma spectrometry

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Abstract Combination of alpha and gamma spectrometry for air filters measurement allows a simple determination of all short-lived ^{222}Rn and ^{220}Rn daughters as well as cosmogenic ^{7}Be and anthropogenic ^{137}Cs in the air. Solid radionuclides in the atmosphere, attached to aerosol particles, were collected on filters of High Volume Air Sampler. After the desired collection period, the activity of deposited radionuclides was measured by γ-spectrometry for ^{7}Be, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi and by α-spectrometry for ^{212}Po, ^{214}Po and ^{218}Po. Spectrometric methods do not require additional sample preparation and allow one to find aerosol activity by a simple filter measurement. A special measurement and calculation procedure was applied in the case of radionuclides from the uranium and thorium series. A technique of liquid scintillation counting (LSC) was used to determine the activity of the long-lived radon daughters ^{210}Pb, ^{210}Bi, ^{210}Po after leaching into HCl solution and a two-step pre-concentration. Simultaneous determination of ^{210}Pb and ^{210}Bi enables one to find aerosol residence times.

Key words aerosol activity determination • aerosol residence times • liquid scintillation counting • radon daughters • α-spectrometry • γ-spectrometry

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Introduction

Primordial cosmogenic or anthropogenic radionuclides present in the ambient air are useful tracers for studying physical and health-related processes in the atmosphere [5]. Especially, the knowledge of the ^{222}Rn and ^{220}Rn daughters concentration in surface air is important as these radionuclides are responsible for a large fraction of the total public exposure to ionizing radiation. On the other hand, the activity ratios of radon daughters, ^{210}Bi/^{210}Pb or ^{210}Po/^{210}Pb are often used for calculation of aerosol residence times in the surface air and troposphere [10].

Solid radionuclides in the atmosphere – the radon progeny as well as ^{7}Be – are usually attached to aerosol particles. Therefore, radioactivity determination of particulates collected on filters of High Volume Air Sampler is a standard technique for monitoring airborne activity [9, 13, 14]. After the desired collection period the activity of deposited radionuclides can be measured by γ-spectrometry for ^{7}Be, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi or by α-spectrometry for ^{212}Po, ^{214}Po and ^{218}Po. Spectrometric methods do not require additional sample preparation and allow one to find aerosol activity by a simple filter measurement.

However, in the case of radionuclides from the uranium and thorium series a special measurement and calculation procedures must be applied [3, 6, 7]. The reason is the change in number of their atoms on a filter during sampling and counting, according to the law of radioactive decay for secular and transient parent-daughter equilibrium.

The mathematical relations between the radionuclide activity on a filter and its concentration in the air for short-lived radon daughters can be simplified by combining α- and γ-spectrometry methods and measurement of the total number of disintegrations instead of decay rate.

Additionally, after nondestructive instrumental measurement the activity of long-lived radon daughters, ^{210}Pb, ^{210}Bi and ^{210}Po, can be determined on the same filter by liquid scintillation counting (LSC). This demands leaching of the collected radionuclides into a solution. There are several methods of separation and pre-concentration of these nuclides, e.g.: co-precipitation with calcium phosphate [1], ion exchange [9], extraction with special cocktails [13] or solid phase extraction [8]. Combinations of these methods give better results, for example, co-precipitation followed by selective extraction [2]. The technique of LSC with pulse shape analysis allows one to determine simultaneously the concentrations of ^{210}Pb, ^{210}Bi and ^{210}Po. The activity of ^{210}Pb can be measured directly or calculated from the activity of its progeny ^{210}Bi or ^{210}Po after reaching secular equilibrium (30 day waiting period). The simultaneous determination of ^{210}Pb and ^{210}Bi concentrations enables one to find aerosol residence times.

Experimental

Sampling

The aerosol samples were collected in the center of Lodz 5 m above the ground level in winter-spring time using a High Volume Air Sampler type JAP/T (Münchener Apparatebau, Germany) equipped with glass fiber filters (10 cm in diameter). Approximately 200 m^3 and 1500 m^3 of air was filtered for the sample during 3 or 24 h collecting time, respectively.

Instrumental determination of the filter radioactivity

For ^{218}Po determination a CAM PIPS (2000 mm^2) detector was placed 5 mm from a filter and the activity on the filter was measured during continuous filtration for 30 min in two working channels (for ^{218}Po and ^{214}Po) using a TRIS-TAN 1000 Multichannel Analyzer (POLON) (Fig. 1). The measurement started 30 min after the beginning of filtration (to reach ^{218}Po equilibrium on the filter).

The absolute detection efficiency for alpha particles emitted from particulate air matter in the filter was determined by measuring the standards of ^{241}Am co-precipitated with ferric hydroxide. The observed surface densities of the captured dust layer were in the range 0.3÷1.0 mg/cm^2. Therefore, we prepared a set of standards for densities ranging from 0.35 to 0.96 mg/cm^2. The average alpha detection efficiency of ^{241}Am in filters was 15%. The ^{241}Am radionuclide is usually chosen for determining the efficiency of alpha detection as its alpha particle energy – 5.49 MeV is close to 6.00 MeV for ^{218}Po [4].

In practice, two instrumental sampling and counting procedures were applied for short- and long-lived radionuclides, respectively:
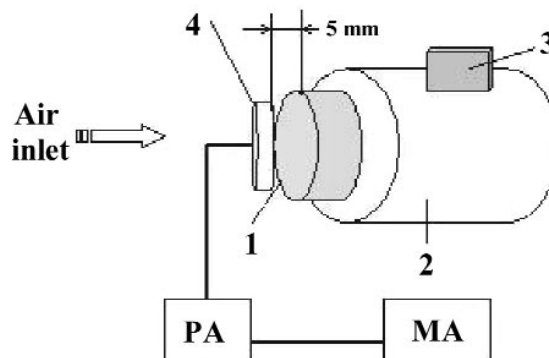

Fig. 1. Air filtration and α-spectroscopy system. 1 – quartz or glass filter; 2 – fan; 3 – air flow meter; 4 – CAM PIPS detector; PA – preamplifier; MA – Multichannel Analyzer TRISTAN 1000.

A – 3 h filtration of air with measurement of ^{218}Po activity, followed by immediate 3 h simultaneous α- and γ-spectrometry counting of the filters for determination of ^{214}Po, ^{214}Bi and ^{214}Pb activities using a Canberra spectrometer with a REGe detector (Fig. 2).

B – 24 h filtration of air followed by simultaneous α- and γ-spectrometry measurement:
   – determination of ^{214}Po, ^{214}Bi and ^{214}Pb activities after 3 h counting,
   – determination of ^{212}Pb, ^{212}Bi, ^{7}Be and anthropogenic ^{137}Cs after further counting for a total period of 2.4×10^5 s (~3 days).

The absolute activities of gamma emitting radionuclides were calculated using an appropriate computer software. For this purpose, the plot of detection efficiency *vs.* energy of γ rays was obtained, using the Multigamma SMR-1 (Amersham) standard solution uniformly deposited on the filter with dust.

Radiochemical determination after the instrumental step

Determination of ^{210}Pb concentration in air by an instrumental method after filtration of only 1500 m^3 of air was impossible due to a relatively high background in the region of 46 keV in the γ-spectrometry system. Activities of ^{210}Pb, ^{210}Bi and ^{210}Po were measured using a LSC technique with pulse shape analysis. For this purpose, after the instrumental step a radiochemical elution of these isotopes was applied.
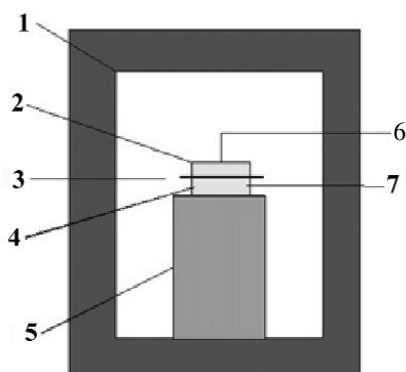

Fig. 2. Air filter measuring system. 1 – lead shielding; 2 – CAM PIPS detector; 3 – air filter; 4 – REGe detector; 5 – dewar with liquid nitrogen; 6 – output of the α-spectrometry system for ^{212}Bi, ^{212}Po, ^{214}Po, ^{218}Po; 7 – output of the γ-spectrometry system for ^{7}Be, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi.

Filters were cut into small pieces and leached by shaking with 300 ml of 2 M HCl for about 30 min. In this procedure, the total amount of ^{210}Pb, ^{210}Bi and ^{210}Po was removed from filters. The solution obtained was filtered to separate a filter or particle residues. The eluted radionuclides were pre-concentrated by alkaline co-precipitation with calcium phosphate at pH=10. To each sample 50 mg of Ca^{2+} ions in the form of calcium chloride and 1 ml of concentrated phosphoric acid were added. Alkalization was proceeded with a concentrated ammonia solution. The obtained precipitate, after centrifugation, was dissolved in 10 ml of 0.3 M HCl with 0.1 ml of H_3PO_4 (85%). The concentrated solution of radionuclides was extracted twice with 5 ml of 0.5 M solution of tri-n-octylphosphine (TOPO) in toluene. The extraction yields of ^{210}Bi and ^{210}Po were 100%. Lead remained almost entirely in the aqueous phase [12]. After phase separation, 95% of the organic scintillator was transferred into small glass vials and 10 ml of a scintillation cocktail Ultima Gold AB (Canberra) was added to each sample (Ultima Gold AB improves α/β separation during LSC activity determination). The samples were counted twice: in alpha $A(^{210}$Po) and in beta $A(^{210}$Bi) mode for 20,000 s in a liquid scintillation counter LKB 1219 Rackbeta (Wallac) in the fixed channels and with the chosen optimal α/β separation settings with the minimum spillovers of the α pulses of ^{210}Po to the β counting channel and β pulses of ^{210}Bi to the α counting channel. The activity of ^{210}Pb $A(^{210}$Pb) was determined after the second extraction of ^{210}Bi with TOPO from the aqueous solution after 4 weeks, when the secular equilibrium between ^{210}Pb and its progeny had been settled.

Calculations of the radionuclide concentration in air

During sampling at a constant air flow V, the change in the number of radionuclide atoms on a filter with time is described by the following differential equation:

$$(1) \qquad \frac{dN_{fi}}{dt} = \frac{A_i \cdot V}{\lambda_i} - \lambda_i \cdot N_{fi}$$

where: N_{fi} – the number of atoms of the i-th nuclide on the filter, λ_i – the decay constant of this nuclide (s^{-1}), V – sampling flow rate (m^3/s), A_i – the air activity of i-th radionuclide (Bq/m^3).

The solution of this equation leads to the following expression:

$$(2) \qquad A_i = A_{fi} \cdot \lambda_i \cdot V^{-1} \cdot \left(1 - e^{-\lambda_i \cdot t_f}\right)^{-1}$$

where: A_{fi} – the activity of i-th radionuclide on a filter (Bq), t_f – filtration time (s).

On the basis of this equation the radionuclide concentrations in air can be simply calculated from the measured activities of ^{7}Be, ^{212}Pb or ^{218}Po on the filter.

In the case of short-lived ^{222}Rn daughters: ^{218}Po, ^{214}Pb, ^{214}Bi or ^{212}Bi (^{220}Rn daughter) a general equation for the activity change of the collected radionuclides during filtration must be used:

$$(3) \qquad \frac{dN_{fi}}{dt} = \frac{A_i \cdot V}{\lambda_i} - \lambda_i \cdot N_{fi} + \lambda_{i-1} \cdot N_{f(i-1)}$$

After 24 h filtration when the transient radioactive equilibrium is settled one can get:

$$(4) \qquad A_{f1} = \frac{A_1 \cdot V}{\lambda_1} \qquad \text{for } ^{218}\text{Po } (i=1)$$

$$(5) \qquad A_{f2} = \left(\frac{A_1}{\lambda_1} + \frac{A_2}{\lambda_2}\right) \cdot V \qquad \text{for } ^{214}\text{Pb or } ^{212}\text{Bi } (i=2)$$

$$(6) \qquad A_{f3} = \left(\frac{A_1}{\lambda_1} + \frac{A_2}{\lambda_2} + \frac{A_3}{\lambda_3}\right) \cdot V \qquad \text{for } ^{214}\text{Bi } (i=3)$$

The activities of these radionuclides on a filter at the end of filtration can be simply determined by γ- (^{214}Bi, ^{214}Pb) or α-spectrometry (^{218}Po) not by the direct measurements as they change rapidly during the counting, but by determination of the total number of disintegrations I_i from the end of filtration to the complete decay of a particular radionuclide. In such case the following set of equations is valid:

$$(7) \qquad A_{f1} = \frac{\lambda_1 \cdot I_1}{E_1}$$

$$(8) \qquad A_{f2} = \lambda_2 \cdot \left(\frac{I_2}{E_2} - \frac{I_1}{E_1}\right)$$

$$(9) \qquad A_{f3} = \lambda_3 \cdot \left(\frac{I_3}{E_3} - \frac{I_2}{E_2}\right)$$

where E_1, E_2 and E_3 denote the absolute detection efficiencies of ^{218}Po, ^{214}Pb and ^{214}Bi, respectively.

The combination of Eqs. (7–9) and (4–6) allows one numerical calculation of radionuclide concentration A_1, A_2 and A_3 from the measured total number of their disintegrations on the filter. This procedure can be applied for all radionuclides in secular radioactive equilibrium with reasonably long half-lives (<12 h).
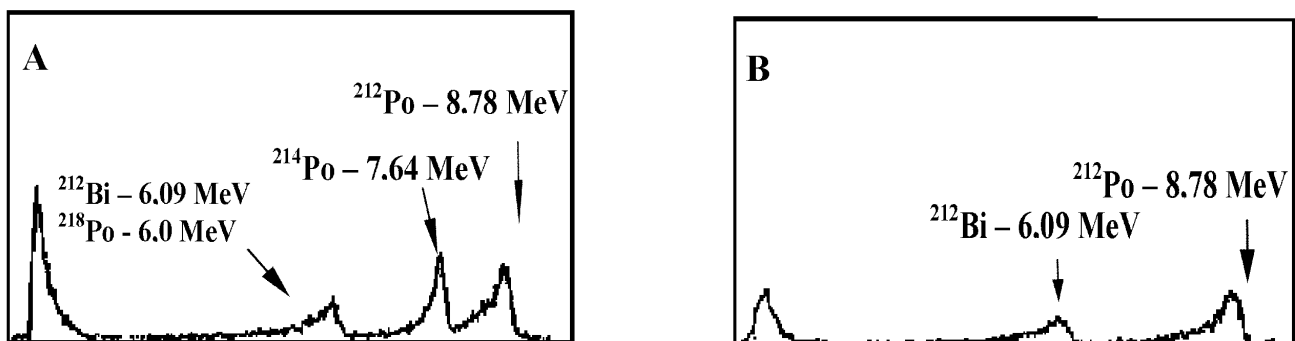

Fig. 3. The α spectra of a typical air filter obtained after 24 h filtration. A – 24 h filtration, 1 min delay time, 3 h counting (with a metal net collimator); B – 24 h filtration, 3 h delay time, 3 counting (with a metal net collimator).

The residence time τ_R of aerosol particles can be calculated from the ratio of activities of genetically-related isotopes [9], e.g. by using the following equations:

$$(10) \qquad A = \frac{A\left(^{210}\mathrm{Bi}\right)}{A\left(^{210}\mathrm{Pb}\right)}$$

$$(11) \qquad \tau_R = \frac{1}{\lambda_{Bi}} \cdot \frac{A}{1-A}$$

where $A(^{210}\mathrm{Bi})$ and $A(^{210}\mathrm{Pb})$ denote the activities of $^{210}\mathrm{Bi}$ and $^{210}\mathrm{Pb}$ in the air particulate matter.

Results

The α spectra obtained with the use of an additional metal net collimator recommended for improvement of the alpha energy resolution are presented in Fig. 3. The spectra have reasonable resolution, and allow one to estimate the activity of selected radionuclides. As it is shown in Fig. 3, after 24 h of collection, for the first 3 h of counting three main peaks can be observed: 6.09 MeV for $^{212}\mathrm{Bi}$ and $^{218}\mathrm{Po}$ (the 6.0 for $^{218}\mathrm{Po}$ can be hardly separated), 7.64 MeV for $^{214}\mathrm{Po}$ and 8.78 MeV for $^{212}\mathrm{Po}$. Assuming that the short-lived radionuclides $^{218}\mathrm{Po}$ and $^{214}\mathrm{Po}$ decay entirely during the first 3 h of counting, only two peaks of longer lived isotopes ($^{212}\mathrm{Bi}$ and $^{212}\mathrm{Po}$) can be noticed after 3 h delay.

However, for a short collection period of 3 h, the identification of $^{218}\mathrm{Po}$ in the continuous part of the low energy spectrum is impossible because of the remarkable decrease in the detection efficiency below 1%, caused by a severe absorption of the alpha radioactivity by the resolution-improving metal net collimator. Therefore, for a short filtration period of 3 h, $^{218}\mathrm{Po}$ was determinated using the PIPS detector without that collimator.

The typical spectrum of α radioactivity collected on the filter during continuous filtration is shown in Fig. 4. Because of much worse resolution, the contribution of $^{214}\mathrm{Po}$ to the $^{218}\mathrm{Po}$ activity in the first channel must be considered. Some of the determination results of short-lived radon daughters, according to the procedure A, are presented in Table 1.

Additionally, the equilibrium concentration of the radon daughters, which is used for dosimetry purposes can be calculated according to the generally accepted formula [11]:

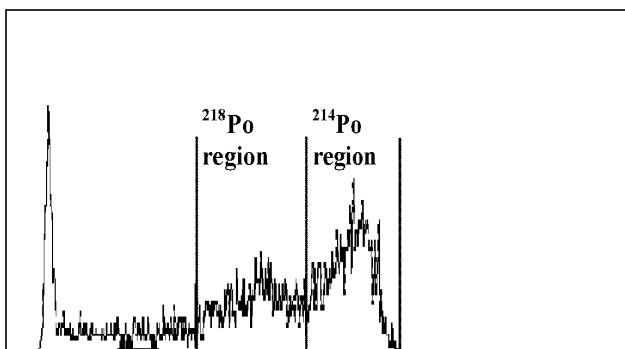$$(12) \qquad C_{eq} = 0.105 \cdot A_1 + 0.516 \cdot A_2 + 0.379 \cdot A_3$$

Fig. 5a. Fluctuations in $^{214}\mathrm{Pb}$ and $^{214}\mathrm{Bi}$ concentrations in the surface air in Lodz (winter–spring 2000), measured by γ-spectrometry.
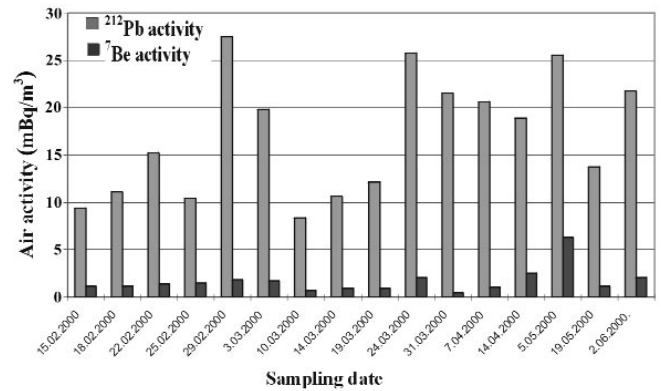
Fig. 5b. Fluctuations in $^{212}\mathrm{Pb}$ and $^{7}\mathrm{Be}$ concentrations in the surface air in Lodz (winter–spring 2000), measured by γ-spectrometry.
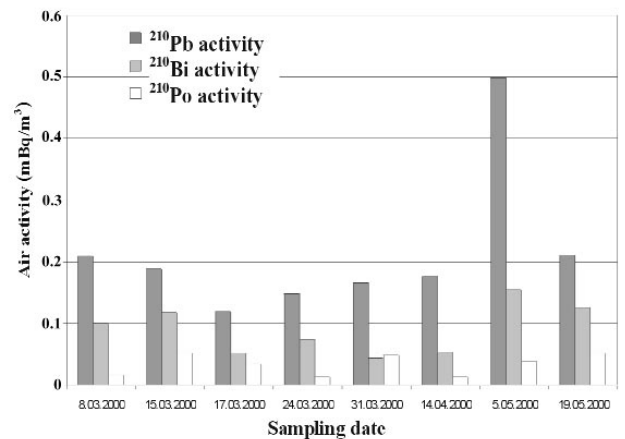
Fig. 6. Fluctuations in $^{210}\mathrm{Pb}$, $^{210}\mathrm{Bi}$ and $^{210}\mathrm{Po}$ concentrations in the surface air in Lodz (winter–spring 2000), measured by LSC technique.

Fig. 4. The α-spectra of a typical air filter obtained during continuous filtration (without metal net collimator). The measurement started 30 min after the beginning of filtration.
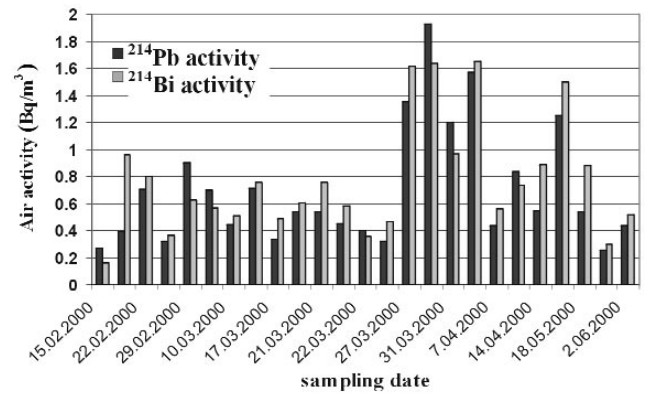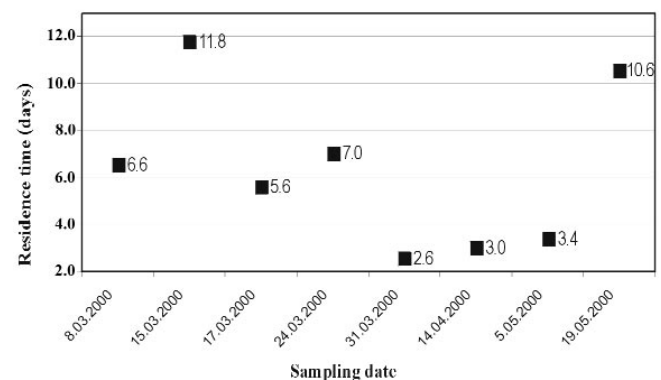
Fig. 7. Aerosol residence times calculated from the $^{210}\mathrm{Bi}/^{210}\mathrm{Pb}$ activity ratio.

Table 1. Determination of the concentration of the short-lived radon daughters in outdoor air.

Sample code	A_1(^{218}Po) (Bq/m^3)	A_2(^{214}Pb) (Bq/m^3)	A_3(^{214}Bi) (Bq/m^3)	C_{eq} (Bq/m^3)
WH13	1.26	0.54	0.56	0.62
WH15	0.32	0.51	0.54	0.50
WH16	0.98	0.27	0.44	0.41
WH23	1.28	0.45	0.41	0.52
WH24	0.81	0.43	0.43	0.47

The results of γ-spectrometry measurements according to the procedure B and the calculations for ^{214}Bi, ^{214}Pb, ^{212}Pb and ^{7}Be are shown in Figs. 5a and 5b. Figure 6 presents the results of LSC measurements for ^{210}Pb, ^{210}Bi and ^{210}Po.

The radionuclide concentrations observed vary widely depending on weather conditions (snow, rain, wind, humidity). Relatively low activities of the ^{222}Rn and ^{220}Rn daughters in the ambient air result from the low concentrations of their mother radionuclides, ^{226}Ra and ^{232}Th, in the soil in the Lodz region [2]. The determined activities of ^{210}Bi and ^{210}Pb were used for the calculation of aerosol residence times. The calculation results of are presented in Fig. 7.

Discussion

The γ-spectrometry measurements have some advantages over α-spectrometry: much better energy resolution (for REGe detectors) and a simple calibration of detection efficiency (independent of the mass of the air particulate matter). However, a few important radionuclides, in particular ^{210}Po, ^{214}Po and ^{218}Po are pure α emitters. The combination of alpha and gamma spectrometry for air filters allows the simple determination of all short-lived ^{222}Rn daughters as well as cosmogenic ^{7}Be and anthropogenic ^{137}Cs in air. After the spectrometry measurements, the filters can also be used for radiochemical determination of the long-lived ^{222}Rn daughters, ^{210}Pb, ^{210}Bi and ^{210}Po, and for the calculation of aerosol residence time.

The observed generally small disequilibrium in the ^{214}Pb-^{214}Bi concentrations can be explained by the errors of activity measurements. In the case of ^{218}Po activity calculation (Table 1) that error is much higher because of the remarkable ^{214}Po interference caused by the poor alpha energy resolution for the filter samples. However, the contribution of the ^{218}Po activity to the total equilibrium radon concentration is about 10% only.

The measured activities of radionuclides in the surface air in Lodz during winter-spring time show typical fluctuations in the ranges similar to those reported in the literature [5, 12, 14]. One can hardly observe the influence of the seasonal increase of the air particulate matter levels around large local coal-fired power plants on the specific activity of selected nuclides. It seems that climatic conditions have a substantial impact on the radionuclide concentrations as well as on the aerosol residence times.

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