DETERMINATION OF ^{210}Pb AND ^{210}Po IN ENVIRONMENTAL SAMPLES

Ljudmila Benedik, Polona Vreček

Jožef Stefan Institute, Department of Environmental Sciences, Jamova 39, 1000 Ljubljana, Slovenia;
e-mail: ljudmila.benedik@ijs.si

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Abstract

The naturally-occurring radionuclides ^{210}Pb and ^{210}Po (22.3 y and 138.4 d half-lives, respectively), are important because of their contributions to the natural radiation dose and release into the environment from technologically-enhanced sources. Methods for determination of ^{210}Pb and of ^{210}Po are described. Both radionuclides were determined in waters and in air filter samples. The procedure for determination of ^{210}Pb includes dithizone extraction for the separation of lead from the matrix and precipitation of $PbCrO_4$ with $K_2Cr_2O_7$ from weak acetic acid media. After waiting for radiochemical equilibrium to be re-established between ^{210}Pb and its daughter ^{210}Bi (at least 20 days), the activity of ^{210}Bi was measured on a gas flow proportional beta counter. The method for determination of ^{210}Po is based on spontaneous deposition of polonium radioisotopes on a copper planchet and measurement by alpha spectrometry. Both methods were optimised using ^{208}Po and ^{212}Pb tracers. A procedure for preparation of ^{212}Pb tracer that involves purging of thorium nitrate solution with nitrogen was developed.

Introduction

^{210}Pb and ^{210}Po are members of the uranium-radium decay chain. ^{210}Pb has a half-life of 22.3 years and is a beta emitter. Its daughter ^{210}Bi is also a beta emitter. Its grand-daughter ^{210}Po is an alpha emitter, with a half-life of 138.4 days which decays further to stable ^{206}Pb. $^{210}\text{Pb}\ (\gamma\beta^-) \rightarrow {}^{210}\text{Bi}\ (\beta^-) \rightarrow {}^{210}\text{Po}\ (\alpha) \rightarrow {}^{206}\text{Pb}$ (stable).

In areas where uranium is mined and extracted, ^{210}Pb and ^{210}Po may accumulate in tailings and run-off, resulting in higher concentrations in the biosphere. Besides this, some anthropogenic sources exist; associated with phosphate fertilisers, fossil fuel burning power plants, lead production, cement manufacture and fallout from nuclear weapon tests. High levels of ^{210}Po are also known to occur naturally in deep-sea fish, shell fish and reindeer or caribou meat.[1]

The natural nuclides ^{210}Pb, ^{210}Bi and ^{210}Po, which originate in the emanation of the rare-gas nuclide ^{222}Rn from land surfaces, are of great importance. ^{222}Rn is a noble gas, diffusing through fissures to aquifer layers, where its long-lived products can be dissolved. These radionuclides are important components of the natural radiation exposure. According to dose factors given by ICRP Publication 67 [2], very low limits for derived activity concentrations in drinking water would be obtained, if all these radionuclides were taken into account. The absorbed doses from the ^{210}Pb sub-series depend mainly on the highly energetic alpha particles of ^{210}Po, as the contribution from the beta emissions of ^{210}Pb and ^{210}Bi amounts to about 10% of the total. The annual effective dose equivalent arising from the total intake of ^{210}Pb, ^{210}Bi and ^{210}Po would be about 130 μSv. This fact demands reliable analytical techniques for analyses of biospheric samples in potentially exposed areas.[3]

Procedures which involve the spontaneous deposition of ^{210}Po from acidic media onto a less noble metal such as Cu, Ag or Ni are commonly used for the isolation of both trace and macrolevels. Radiochemical determination of ^{210}Pb is usually accomplished by measuring the beta activity of its ^{210}Bi daughter ($E_{\beta max.}$= 1.17 MeV) or the alpha activity of its ^{210}Po granddaughter (E_α = 5.32 MeV).This is because direct determination of ^{210}Pb is difficult due to its low gamma energy (E_γ = 0.047 MeV of low abundance (4.05 %)) and the low energy of its beta emission ($E_{\beta max.}$= 0.06 MeV). Since it is the daughter or granddaughter radionuclide that is isolated and quantitatively measured, it is necessary to know the degree of equilibrium that exists between the progeny and its parent ^{210}Pb. For ^{210}Bi (half-life 5.01 days) an equilibrium of greater then 98% is established in 30 days. For ^{210}Po (half-life 138.4 days) a period of over 4.5 months is required to reach 50% and 18 months to reach 88% ingrowth. Despite the fact that alpha spectroscopic measurement of the in-grown ^{210}Po, often using ^{208}Po as a tracer, can achieve an ultra-low detection limit, the long ingrowth period required to achieve this makes it an impractical method when rapid low level measurements are required. In these circumstances a procedure for the isolation and measurement of the ^{210}Bi daughter is preferred. In separation of ^{210}Pb, the naturally occurring radiotracer ^{212}Pb (half-life 10 h) is often used to determine the chemical yield. Preparation of pure tracer ^{212}Pb is very important, because impure tracer could contaminate the sample with beta emitters that interfere in the measurement of ^{210}Bi on a beta counter. A method for preparation of ^{212}Pb tracer that includes extraction of thorium nitrate solution with dithizone in chloroform is known.[4,5,6] Small amounts of other radionuclides from the thorium decay chain are also extracted making the ^{212}Pb tracer impure. This paper describes a alternative procedure for ^{212}Pb preparation.

Determination of ^{210}Pb and ^{210}Po activities in water samples in the vicinity of the former uranium mine at Žirovski vrh in Slovenia is important in monitoring environmental contamination and ensuring radioecological protection. Determination of both radionuclides in the local streams Todraščica and Brebovščica is a part of the environmental monitoring programme. Measurement of the activities of ^{210}Pb and ^{210}Po in air filters from the Šoštanj thermal power plant is also presented.

Experimental

Samples

Water samples for ^{210}Pb and ^{210}Po analysis were collected from the local streams Todraščica and Brebovščica. The samples were collected every day and immediately after sampling subjected to filtration (0.45 μm) and acidified by addition of 3 mL nitric acid per litre. We carried out analysis of ^{210}Pb in one-month composite samples and ^{210}Po in three-month composite samples.

Air filters were collected from the chimneys 4 and 5 of the Šoštanj thermal power plant.

Determination of ^{210}Pb

1. Radiochemical separation

To determine very low concentrations of ^{210}Pb in water samples the radionuclide should be first concentrated by evaporation. 6 L of water sample was taken, 0.2 mg Pb^{2+} (lead carrier) was added, the sample evaporated to dryness and the residue dissolved in 50-100 mL 6 M hydrochloric acid. Two analytical steps in the procedure for the determination of ^{210}Pb were then used:

a) dithizone extraction for the separation of lead,

b) precipitation of $PbCrO_4$ with $K_2Cr_2O_7$ from weak acetic acid media.[7]

5 mL of 1 M solution of sodium citrate that prevents the precipitation of hydroxides and 1 mL of a 10% solution of potassium cyanide that masks II and III

valent ions were added. pH was adjusted to 8.5-10 with ammonia solution. After that extraction of lead with 10-15 mL of a 0.005% solution of dithizone in chloroform was performed. The organic phase was then evaporated and the residue diluted in 60 mL of distilled water. Then 20 mg of Pb^{2+} and 1 mL of concentrated acetic acid were added and the pH adjusted to 4-5 with ammonia solution. The solution was heated, and $PbCrO_4$ precipitated by addition of 1 mL of 1M $K_2Cr_2O_7$. The precipitate was then plated on a measuring planchet by centrifugation. After waiting for radiochemical equilibrium to be re-established between ^{210}Pb and ^{210}Bi (at least 20 days), the activity of ^{210}Bi beta emission was measured on a gas flow proportional beta counter (Berthold MULTI-LOGGER LB 5310). The activity of ^{210}Pb was calculated from Equation 1.

$$A_{Pb} = \frac{A_{Bi}}{(1-e^{-\lambda_{Bi} \cdot t}) \cdot \eta \cdot \varepsilon_{\text{det.}} \cdot V_s} \qquad \textit{Eq. 1}$$

A_{Pb}	activity of ^{210}Pb in sample in Bq m^{-3}
A_{Bi}	activity of ^{210}Bi in Bq
λ_{Bi}	1.605×10^{-6} s^{-1}
t	time of the ^{210}Bi regrowth (s)
η	overall recovery
$\varepsilon_{det.}$	counting efficiency
V_s	sample volume in m^3

2. Preparation of ^{212}Pb tracer

To determine the overall recovery (η) and also to perform experiments to optimise the radiochemical procedure the radioactive tracer ^{212}Pb was used. Equipment for its preparation is presented in Figure 1.

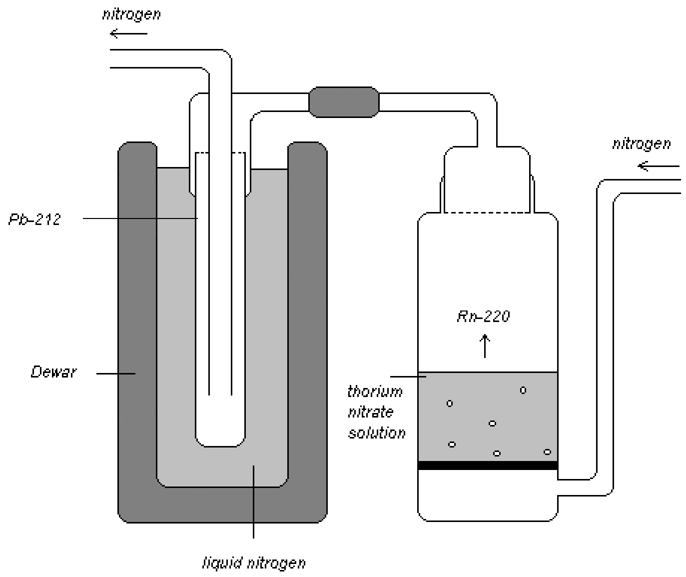

Figure 1: Equipment for ^{212}Pb tracer preparation.

The right hand part of the equipment contained a thorium nitrate solution (100 g $Th(NO_3)_4$ in 100 mL). This solution was purged by nitrogen for 10 hours at a flow rate of about 20 mL min^{-1}. ^{220}Rn that was removed from the solution is a short-lived (half-life of 55.6 s) member of the thorium decay chain and decays via its daughter ^{216}Po further to ^{212}Pb. The left hand part of equipment was cooled with liquid nitrogen to trap volatile ^{220}Rn. The decay product ^{212}Pb was collected on the glass walls from which it was washed with a 0.5 M solution of HCl. ^{212}Pb prepared in this way was observed to be very pure. Its purity was checked using gamma spectrometry and beta counting. A filter to trap any possible carry-over of spray containing $Th(NO_3)_4$ was found to be unnecessary. After preparation of ^{212}Pb tracer its initial gamma activity ($E_{\gamma 1}$ = 238.6 keV (43.6 %), $E_{\gamma 2}$ = 300.0 keV (3.3 %)) was measured on a gamma spectrometer.

3. Optimisation of experimental parameters

As mentioned above some parameters required in the procedure for determination of ^{210}Pb were determined in a series of experiments and optimised using ^{212}Pb tracer. We determined the optimal time of extraction, the overall recovery and the experimental stoichiometric factor.

The gravimetric yield of precipitation, the experimental stoichiometric factor and the overall recovery were calculated from Equations 2.

The gravimetric yield of precipitation is determined by weighing the lead chromate precipitate. We presumed that lead precipitates only in lead chromate form (but see below).

The chemical yield of precipitation is determined using ^{212}Pb tracer. A known amount of ^{212}Pb tracer was added to deionised water to perform just the precipitation step. The gamma activity of ^{212}Pb in lead chromate form was measured by gamma spectrometry. The chemical yield of precipitation was then calculated as the ratio between the activity of ^{212}Pb added and activity of ^{212}Pb found in lead chromate.

The overall recovery was calculated as the product of the chemical yield of extraction and the chemical yield of precipitation.

The stoichiometric factor is the ratio between the mass of Pb in the precipitate and the mass of the precipitate. If lead would precipitate only in lead chromate form, the stoichiometric factor would be 0.6411. An experimental stoichiometric factor was determined because the precipitate of lead chromate has a nonstoichiometric composition, since it also includes chromate ions and at pH lower than 5 lead does not precipitate only in the form of lead chromate but also in the form of lead dichromate. Non-stoichiometry is due to the presence of chromate ions and lead dichromate.

$$\eta_{gr.} = \frac{m_{Pb} \cdot 0.6411}{20\ mg} \quad ; \quad f = \frac{\eta_p}{\eta_{gr.}} \cdot 0.6411 \quad ; \quad \eta = \eta_e \times \eta_p \qquad \textit{Eq. 2}$$

η_{gr}	gravimetric yield of precipitation
m_{Pb}	mass of lead chromate precipitate
0.6411	stoichiometric factor for lead chromate precipitate
f	experimental stoichiometric factor
η_p	chemical yield of precipitation
η	overall recovery
η_e	chemical yield of extraction

4. Efficiency of the gas flow proportional counter

The counting efficiency of ^{210}Bi on the beta counter was determined with a known amount of solid KCl (0.0117 % ^{40}K, E_β = 1505 keV) and with ^{210}Pb standard solution evaporated on a lead chromate precipitate (^{210}Bi, E_β = 1161 keV).

Determination of ^{210}Po

1. Radiochemical separation

The treatment of a water sample is very similar to the treatment of the sample for determination of ^{210}Pb. The difference is in the amount of sample (15 L) that was taken and in the addition of ^{208}Po tracer in the first stage. To separate polonium, the technique of spontaneous deposition of polonium radioisotopes on a copper planchet for four hours at 50°C and pH 1 was performed. The equipment for spontaneous deposition of polonium radioisotopes is presented in Fig.2. The sample solution after evaporation to small volume, adjusted to pH 1 with hydrochloric acid, was put into the beaker together with the holder and copper planchet. The sample solution at 50°C must be stirred continuously during spontaneous deposition.[8]

Then polonium radioisotopes were measured by alpha spectrometry (Tennelec TC 256 alpha spectrometer) and the activity of ^{210}Po was calculated from Equation 3.

$$A_{Po} = \frac{Area_{Po}}{t \cdot \eta_{chem.} \cdot \eta_{det.} \cdot V_s} \qquad \textit{Eq. 3}$$

A_{Po}	activity of ^{210}Po in water sample in Bq m^{-3}
$Area_{Po}$	peak area for ^{210}Po (decay/s)
T	time of measurement (s)
η_{chem}	yield of ^{208}Po tracer
η_{det}	counting efficiency
V_s	sample volume (m^3)

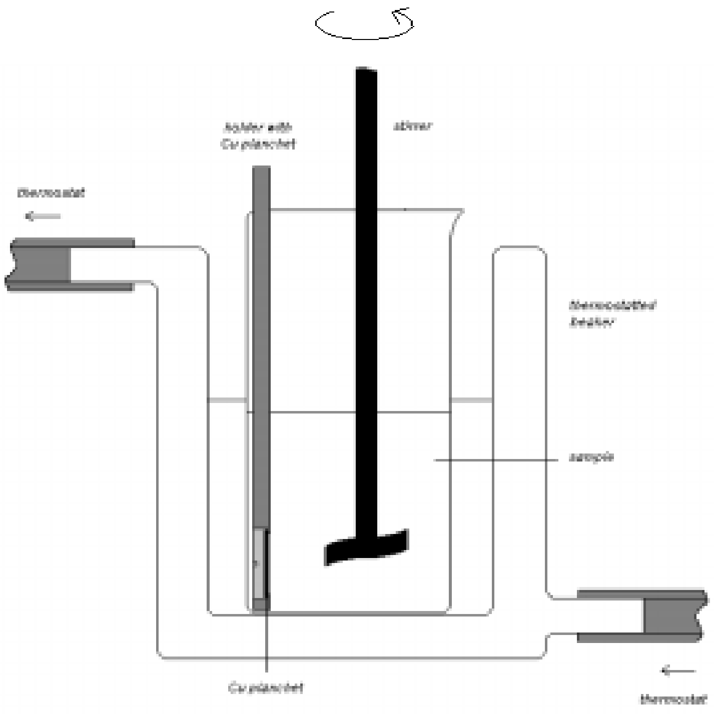

Figure 2: Equipment for spontaneous deposition of polonium radioisotopes.

2. Optimisation of plating time

For optimisation of the procedure for the determination of ^{210}Po the radioactive tracer ^{208}Po was used and the plating efficiency determined as a function of time.

3. Determination of efficiency of alpha detector

The counting efficiency of the α-detector was determined with a calibrated source of ^{230}Th (E_α=4687 keV (76.3 %)).

Determination of ^{210}Pb and ^{210}Po in air filters

Samples of air filters were leached for 24 hours in a solution of 6 M hydrochloric acid together with lead carrier and ^{208}Po tracer. The solution prepared in this way was divided into two equal parts. In one part ^{210}Pb was determined and in the second part ^{210}Po was determined, using the procedures described above.

Results and discussion

Determination of ^{210}Pb

Table 1 shows results obtained for the yield of the first and second extraction of lead by dithizone by ^{212}Pb tracer experiments. In the separation of Pb by dithizone extraction, it can be observed from Table 1 that in 1 minute around 95 % of lead is extracted. Even if the time of extraction is extended, chemical yields are not higher. A second extraction is thus not necessary, because only around an additional 2 % of lead is then extracted.

Table 1: Yield of the first and the second extraction as a function of extraction time.

Time of extraction	Yield of first extraction (%) (n=4)	Yield of second extraction (%) (n=4)
1 min	94.4 ± 1.7	2.4 ± 0.6
2 min	95.8 ± 3.1	1.9 ± 0.4
3 min	95.0 ± 4.9	2.0 ± 0.7
4 min	94.9 ± 1.1	1.4 ± 0.1

Table 2 shows the overall recovery and the experimental stoichiometric factor found for lead chromate precipitation. The overall recovery was determined as 91.9 % and the experimental stoichiometric factor was determined as 0.524.

Table 2: Determination of overall recovery and experimental stoichiometric factor.

Chemical yield of extraction (%) η_e (n=18)	95.4 ± 4.2
Chemical yield of precipitation (%) η_p (n=18)	96.5 ± 5.2
Gravimetric yield of precipitation (%) $\eta_{gr.}$ (n=18)	118 ± 2
Overall recovery (%) η (n=18)	**91.9 ± 3.0**
Experimental stoichiometric factor f (n=18)	**0.524 ± 0.027**

This procedure was then verified by the standard addition method. Tap water samples with different amounts of ^{210}Pb standard addition were prepared. The activity of ^{210}Pb in the sample was found to be 103 mBq, while the standard addition method gave a value of 95.4 mBq. This agreement shows that the method for determination of ^{210}Pb is reliable.

The counting efficiency of the gas flow proportional counter determined with solid KCl (from ^{40}K) and by ^{210}Pb standard solution was 43.1 % and 43 % , respectively. The minimum detectable activity (MDA) of ^{210}Pb was determined using the Currie equation[9]:

$$MDA\ (Bq\ m^{-3}) = \frac{4.65 \cdot S_b + 2.71}{\varepsilon_{\mathrm{det.}} \cdot \eta_{chem.} \cdot t \cdot V} \qquad \textit{Currie equation}$$

S_b the standard deviation of a series of counts of an appropriate blank sample

ε_{det} counting efficiency

η_{chem} chemical recovery

t counting time for the sample (s)

V sample volume (m^3)

In the case of determination of ^{210}Pb in water samples we made a series of 5 experiments with blank samples and determined the MDA as 1.8 ± 0.2 Bq m^{-3} when 6 L of water sample was used.

Tables 3 and 4 show results for the activity of ^{210}Pb in water samples from the Todraščica and Brebovščica streams (year 1998) and activities of ^{210}Pb in water samples from wells in the vicinity of the former Žirovski vrh uranium mine.

Table 3: Activities of ^{210}Pb in samples of Todraščica and Brebovščica streams, 1998.

Sample	Todraščica ^{210}Pb (Bq m^{-3})	Brebovščica ^{210}Pb (Bq m^{-3})
1	14 ± 1	15 ± 2
2	85 ± 9	13 ± 1
3	63 ± 6	23 ± 2
4	68 ± 7	17 ± 2
5	22 ± 2	38 ± 4
6	16 ± 2	21 ± 2
7	23 ± 2	6 ± 1
8	12 ± 1	2.0 ± 0.2
9	16 ± 2	4.9 ± 0.5
10	13 ± 1	3.4 ± 0.3
11	9 ± 1	13 ± 1
12	4.2 ± 0.4	2.8 ± 0.2

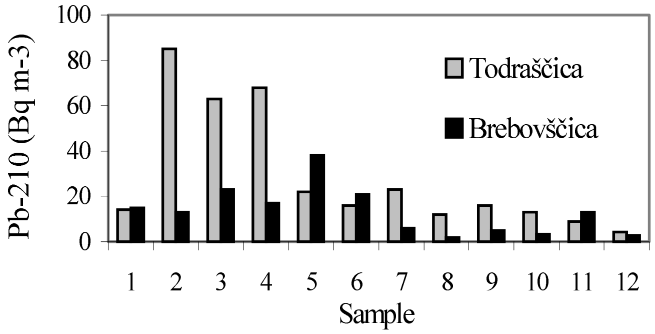

Figure 3: Diagram showing activities of ^{210}Pb for monthly samples of Todraščica and Brebovščica streams,1998.

Table 4: Activities of ^{210}Pb in wells from the vicinity of the former uranium mine at Žirovski vrh.

Sample of water from well	^{210}Pb (Bq m^{-3})
BS-26	5.6 ± 0.6
BS-30	12 ± 1
Drmota	8.4 ± 0.8

Determination of ^{210}Po

The results of the experiments to determine the plating efficiency as a function of plating time are shown in Fig.4. It can be observed that the curve reaches a plateau at around 240 min. At that time around 90 % of polonium radioisotopes are deposited.

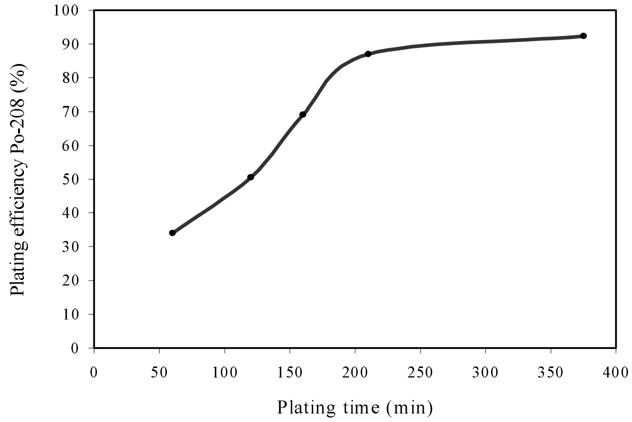

Figure 4: Plating efficiency as a function of plating time in spontaneous deposition of Po radioisotopes on a Cu planchet at 50°C, pH=1.

The counting efficiency of the α-detector was found to be 30.9 %.

For determination of ^{210}Po the MDA was also determined using the Currie equation. The average of 5 experiments with blank samples gave a value of 0.040 ± 0.003 Bq m^{-3} if 15 L of water sample were used.

Table 5 shows results for the activity of ^{210}Po in water samples of the Todrašččica and Brebovščica streams (year 1998).

Table 5: Activities of ^{210}Po in samples of Todraščica and Brebovščica streams,1998.

Sample	Todraščica (Bq m^{-3})	Brebovščica (Bq m^{-3})
1st quarter	3.4 ± 0.2	2.8 ± 0.2
2nd quarter	2.3 ± 0.1	1.8 ± 0.1
3rd quarter	2.3 ± 0.1	1.7 ± 0.1
4th quarter	0.99 ± 0.06	0.86 ± 0.05

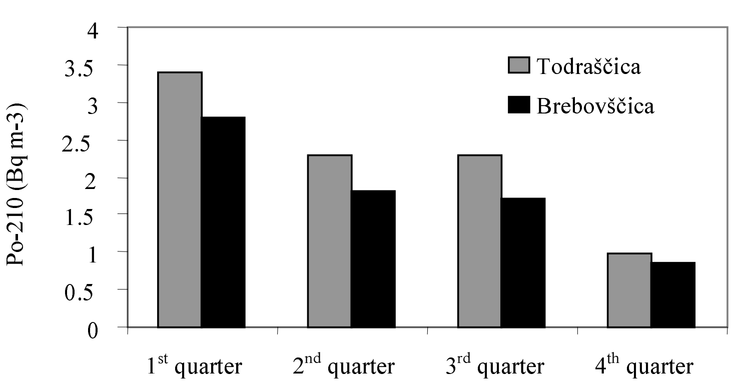

Figure 5: Diagram showing activities of ^{210}Po as a function of season for samples from the Todraščica and Brebovščica streams,1998.

Fig.6 shows an alpha spectrum of polonium radioisotopes separated from a water sample. The spectrum is radiochemically pure; the peaks of ^{210}Po at 5.3 MeV and of ^{208}Po tracer at 5.1 MeV can be observed.

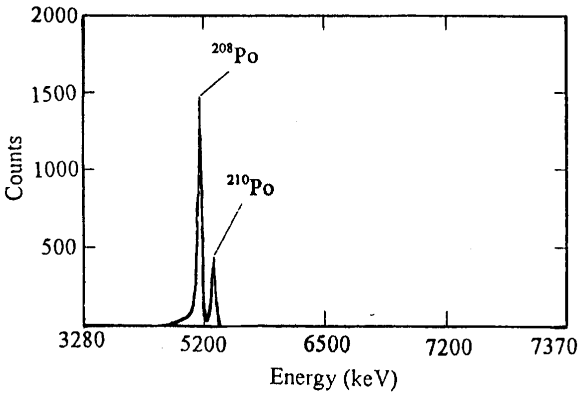

Figure 6: Alpha spectrum of ^{210}Po in sample from the Brebovščica, 3rd quarter, 1998, with ^{208}Po tracer.

Determination of ^{210}Pb and ^{210}Po in air filters

Both radionuclides were also determined in air filters from two chimneys of the Šoštanj thermal power plant. In Table 6 the results are presented. The coal used by the thermal power plant contains relatively high activities of naturally-occurring radionuclides, particularly uranium (~ 100 Bq kg^{-1}). While uranium and radium remain in the ash, polonium and lead, because they are volatile, are released with exhaust gases and contaminate the surroundings. It can be observed that the activities of ^{210}Pb and

^{210}Po in air filters from chimney 4 are much lower than the activities of these radionuclides determined in air filters from chimney 5. That is because in chimney 4 desulphurisation plant to clean the exhaust gases is installed. In this procedure dust is also removed and environmental contamination by volatile radionuclides is successfully reduced.

Table 6: Activities of ^{210}Pb and ^{210}Po in samples of air filters from chimneys 4 and 5 of the Šoštanj thermal power plant.

Sample		Air volume filtered (L)	Dust amount (mg)	^{210}Pb (Bq kg^{-1})	^{210}Pb (mBq m^{-3})	^{210}Po (Bq kg^{-1})	^{210}Po (mBq m^{-3})
4	Filter17	3150	21.4	8685 ± 869	59 ± 6	2949 ± 177	20 ± 1
	Filter18	3417	59.6	2757 ± 276	48 ± 5	1091 ± 65	19 ± 1
5	Filter13	602	38.8	2451 ± 245	158 ± 16	2296 ± 138	148 ± 9
	Filter15	681	26.1	3575 ± 358	137 ± 14	3705 ± 222	142 ± 9

Conclusions

Determination of ^{210}Pb and ^{210}Po in the Todraščica and Brebovščica streams in the vicinity of the uranium mine is part of the regular environmental monitoring programme. Variation of activities of both radionuclides is a consequence of the weather (rainfalls) in this region. Even if activities in some monthly samples are sometimes a little higher, these levels are still under the maximal permitted activity for ^{210}Pb in waters, which is 400 Bq m^{-3}. The maximal permitted activity for ^{210}Po in waters is 2000 Bq m^{-3}. From Table 5 can be observed that the activities of ^{210}Pb in underground waters are very similar to the activities in surface waters.

The method developed for determination of ^{210}Pb is selective and accurate. The overall recovery measured using ^{212}Pb is more than 90 %. The minimum detectable activity (MDA) for a sample size of 6 litres is 1.8 Bq m^{-3}.

A new method was developed for ^{212}Pb tracer preparation. This method is simple and quick and tracer prepared in this way was observed to be pure enough for its use in determination of the yield with routine samples.

The method for determination of ^{210}Po is very reliable and precise. The plating efficiency was about 90 % after four hours plating at 50°C. The minimum detectable activity (MDA) for a sample size of 15 litres is 0.040 Bq m^{-3}.

Both optimised methods were shown to be suitable for routine measurements of water samples and air filters in monitoring programmes around the former Žirovski vrh uranium mine and a coal-fired electricity generating plant, respectively.

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Povzetek

Razvili smo metodi za določanje ^{210}Pb in ^{210}Po v vzorcih iz okolja. Oba radionuklida smo določali v vzorcih vode in zračnih filtrov. Svinec smo separirali z ekstrakcijo z ditizonom in obarjanjem v obliki svinčevega kromata. Po vzpostavitvi radiokemičnega ravnotežja med ^{210}Pb in njegovim potomcem ^{210}Bi smo beta aktivnost ^{210}Bi pomerili na beta proporcionalnem števcu. Polonijeva radioizotopa smo separirali s spontano depozicijo na bakrovo ploščico in le-to pomerili na alfa spektrometru. Obe metodi sta bili optimizirani z uporabo sledilcev ^{208}Po in ^{212}Pb. Uporabili smo postopek za pripravo sledilca ^{212}Pb, ki temelji na prepihavanju raztopine torijevega nitrata z dušikom.