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Study on analytical procedure of plutonium separation from air aerosols collected on Petrianov filter

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Abstract A standard procedure for the determination of plutonium in soil was modified and applied for the assay of this element in dust and aerosols collected from ground-level air on a Petrianov filter, in an ASS-500 air monitoring station. The modification consists in replacing a dry ashing mineralization step by direct acid leaching. The problem of polonium interference with plutonium determination was also discussed and the concentration of polonium in air was estimated.

Key words alpha spectrometry • Petrianov filter • plutonium • polonium

Introduction

Starting from 1993, the measurements of gamma radiation contamination of ground-level air have been conducted weekly in our Department. One of ten air monitoring stations ASS-500 of the Polish early warning system of the Service of Radioactive Contamination Measurements is situated in Lublin, and operated by our research staff with the cooperation of the Central Laboratory of Radiological Protection in Warsaw.

Plutonium isotopes appeared in the environment as a result of nuclear explosions. The Chernobyl release also contributed to the environmental input of transuranium nuclides [3, 10, 12]. At present, most of plutonium introduced into the atmosphere, can be found in the surface layer of soil and in sea sediments. Depending on meteorological conditions, physico-chemical properties of soil and human activity, plutonium isotopes can migrate in the soil environment, enter into plants or become resuspended into air with eroded soil particles. These small soil particles can be trapped on a filter surface.

The literature on plutonium determination in air filters is not large. Cellulose [2] or polycarbonate filters [1, 13, 14] were frequently used, as well as Petrianov filters [4–6, 9]. Usually mineralization of these filters was performed by dry ashing at 450° [1] or 550°C [6, 13, 14] or by wet ashing with concentrated acid mixture [5, 11].

The determination of plutonium isotopes in aerosols and dust collected on a Petrianov filter is connected with the following problems:

– because of small concentration of plutonium, the sample should be composed of several weekly-collected filters,
– for determination of an alpha emitting nuclide a careful chemical separation from the matrix is needed,

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– the Petrianov filter FPP-15-1.5 is made of chlorinated polyvinyl chloride, which hardly submits for thermal or chemical destruction,
– thermal destruction of the FPP leads to liberation of toxic and corrosive gaseous hydrogen chloride.

The aim of this work was to find whether the known method for plutonium determination in soil, applied to Petrianov filters, would produce reliable analytical results.

Methods

Single filter samples from the years 1993 and 1994, and samples of pooled filters from the years 1998 and 1999 were taken for analysis. Method of sample preparation comprised of acid leaching, co-precipitation first with ferric hydroxide and then with calcium oxalate, thermal decomposition of the oxalate, anion exchange separation on Dowex 1×8 (with HCl/HI mixture for Pu elution), and finally electrodeposition onto a stainless steel plate from ammonium oxalate/HCl solution. More details of the procedure are presented elsewhere [7, 8].

Effectiveness of plutonium extraction was determined by adding to the sample a known amount of standard solution of a ^{242}Pu tracer (usually about 0.01 Bq/sample).

Plutonium radioactivity was measured using two alpha spectrometers (Canberra) with PIPS silicon detectors. The System 100 MCA and ASP software was used for quantitative analysis.

Results and discussion

We assumed that direct leaching should be sufficient for the removal of plutonium from the sample and the stage of dry ashing was omitted. The single air filter samples from the years 1993 and 1994 were used to perform this experiment. As the plutonium activity in a single filter was very low, its activity determination was burdened with rather high error. However, determination of the yield of leaching based on ^{242}Pu-tracer added to the sample, produced reliable results even from single filters. Table 1 presents the radiochemical yield of plutonium determination. Among several leaching agents, 6M HCl demonstrates the highest efficiency.

In the plutonium spectra, a high alpha peak at 5.3 MeV of ^{210}Po was observed. Usual separation procedure which should eliminate this radionuclide (anion exchange separation, flame heating of electroplated material to dull red) did not do this in a sufficient degree. Therefore we modified the plutonium separation procedure in order to eliminate polonium. The following modifications were introduced:
– direct elimination of polonium from the solution after acid leaching (a spontaneous deposition of Po on a copper plate from a hot 0.5M HCl solution),
– additional cleaning of the sample with an anion exchanger (repeating step of separation with Dowex 1×8 using HNO_3, HCl and HCl/HI),
– additional separation of plutonium by co-precipitation with calcium oxalate, followed by thermal decomposition of the precipitate (polonium should evaporate as a volatile compound).

Each modification eliminated most of polonium present in the sample. Unfortunately, plutonium spectra were of poor resolution, and the chemical separation yield was low (12% with the first modification used, 24% with the second and 32% with the third).

In other experiments we tried to diminish the uncertainty of plutonium determination by combining several (4–10) single filter samples from the year 1998 to form pooled samples. The samples were treated with 6M HCl, followed by a single co-precipitation with ferric hydroxide and calcium oxalate, anion exchange and finally electrodeposition.

A good separation from other radionuclides except polonium was observed on the spectra and a yield of about 70% was obtained. However, the spectra were of high resolution, and allowed determining plutonium concentration in the samples with an uncertainty of 15%.

These modifications were compared with the standard procedure, which included dry ashing as an initial step. For this purpose, two samples of combined four single filters, from the year 1999 were dry ashed before acidic leaching. Dry ashing was performed by burning the sample in a quartz crucible in a flame of laboratory burner. The ash was leached with 6M HCl and then plutonium was separated. Such mineralization of filters leads to much lower yield than sample leaching. The dry ashed samples in covered crucible revealed the yield of 35%, but without cover only 17%. However, the spectra showed a good resolution. This allowed to determine plutonium concentration in the sample, even in the presence of the ^{210}Po peak.

Because of polonium presence in the alpha radiation spectra, an attempt was made to quantitatively determine this nuclide. Copper plates with spontaneously deposited polonium (after its extraction from three filters from 1993 and 1994) were dried, and submitted to alpha spectrometric measurement. As no polonium tracer was added to the sample there was no possibility to determine the yield of its separation. However, assuming a 100% yield, the amount of extracted polonium ranged from 3.1 to 5.5 Bq per sample. These values were equivalent to 47–65 μBq/m^3.

Polonium was collected directly on the filter as adsorbed on dust particles, or as a product of ^{210}Pb decay. Since 1998 the amount of ^{210}Pb was also determined during gamma radiation measurements of air filter samples. This was possible owing to the use of gamma-ray detector with extended energy range. Taking into account the measured amount of

Table 1. Effect of leaching agents on the yield of plutonium determined in air filters (48 h at room temperature followed by 1 h hot plate).

Number of single filters combined	Leaching agents	Yield [%]
1	6M HCl	67
3	6M HCl	46
1	concentrated HCl/HNO_3	45
1	concentrated HCl/H_2O_2	33
1	concentrated HNO_3/HF/$HClO_4$	19

Table 2. Measured concentration of ^{210}Pb in air filters, amount of ^{210}Po calculated according to Bateman equation and estimated from plutonium spectra (filter samples from 1998, the 100% yield assumed).

Number of single filters combined	^{210}Pb (γ) [Bq/sample]	^{210}Pb (γ) [mBq/m^3]	^{210}Po (calculated) [mBq/m^3]	^{210}Po (from Pu spectra) [nBq/m^3]
4	91.7	0.38	1.42	28
8	122	0.25	0.88	19
10	285	0.36	1.16	25
9	318	0.48	1.28	52
9	361	0.44	1.03	14
4	162	0.75	1.64	55
Mean	223±112	0.44±0.17	1.24±0.27	32±17

^{210}Pb and a time of aerosol collection, the value of ^{210}Po ingrown in the sample was calculated from the Bateman equation for the system ^{210}Pb / ^{210}Bi / ^{210}Po and compared with the amount of polonium found on the alpha spectra. The results are presented in Table 2.

Calculated amount of polonium, ingrown in the sample as a result of ^{210}Pb decay is rather high. However, the polonium initially present in the sample decayed almost completely during the time of storing of the air filter. Therefore all polonium, found in the sample, comes from ^{210}Pb decay. Although the polonium peak is visible in the plutonium spectrum, its amount is negligible in comparison with its original amount, as it is seen in Table 2. The concentration of polonium, estimated from alpha spectra of plutonium, was about 45,000 times lower than that calculated from ^{210}Pb concentration.

Conclusions

The standard method of plutonium separation by leaching with 6M HCl as an initial step (without the stage of dry ashing of the sample) makes it possible to determine the plutonium in the air filter samples. Despite of incomplete separation from polonium, the yield is good enough and peaks of plutonium are well resolved enabling determination plutonium concentration with small uncertainty.

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