DETERMINATION OF ^{210}Po CONTENT IN ENVIRONMENTAL SAMPLES BY ALPHA SPECTROMETRY

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Abstract

Polonium 210 is a naturally occurring alpha-emitting radionuclide, and it can be found in the environment as a progeny of Pb^{210} in the U^{238} decay series. Due to its wide spread and high potential to generate radiation exposure of people, Po^{210} is considered as one of the most radiotoxic natural radionuclides and one of the most important environmental radionuclides. Particular attention was recently paid to polonium, following the increased efforts to develop lead-cooled nuclear reactors. Lead-cooled reactors offer some advantages over other types of fast reactors, but the issue of Po^{210} contamination remains significant. Taking into account the above considerations, the development and implementation of a method for determining the ^{210}Po content represent a requirement for any radiation protection laboratory. This paper presents the results of experimental tests carried out for the selection and implementation of appropriate radioanalytical method to determine, by alpha spectrometry, the content of ^{210}Po in environmental samples.

Keywords: *Po^{210}, environmental samples, alpha spectrometry, ALMERA, IAEA reference materials*

Introduction

Polonium is a metallic element with the atomic number 84, that was discovered by the Pierre and Marie Curie in 1898 when processing uranium ore. The element is soluble in concentrated sulfuric acid, nitric acid, and diluted hydrochloric acid, as well as in several other solutions. It can also form soluble salts with chloride, nitrate, and other inorganic anions. Polonium can have the oxidation states of −2, +2, +4 and +6, oxidation state +4 being stable in solutions.

Polonium has 25 known radioactive isotopes with mass numbers from 192 to 218, and all of them are radioactive, though Po^{208}, Po^{209}, and Po^{210} being the most stable. Po^{210} is a naturally occurring α-emitter with a half-life of 138,4 days and an alpha particle energy of 5.38 MeV. It has high specific activity (1.66×10^{14} Bq/g), high volatility (50% sublimes in a 45-hour interval if maintained at a temperature of 55 ºC and a pressure of one atmosphere), with a low melting temperature (252 ºC), and it can easily form colloids and adsorb on metal surfaces.

Po^{210} exists in the environment as a result of decay via Pb^{210} ($t_{1/2}$ = 22.3 years) and Bi^{210} ($t_{1/2}$ = 5.15 days) in the U^{238} decay series (see below the decay chain of Po^{210}).

$$^{210}Pb \xrightarrow{\beta} {}^{210}Bi \xrightarrow{\beta} {}^{210}Po \xrightarrow{\alpha} {}^{206}Pb(stable)$$

Due to its wide distribution and risks potential for human radiation exposure through ingestion and inhalation, Po^{210} is considered one of the most radiotoxic naturally occurring radionuclides, and one of the most important environmental radionuclides. Po^{210}contribution to the internal radiation dose to human has been estimated to be around 8%.

Taking into account these considerations, development and implementation of a method for determining the Po^{210} content is a requirement for any radiation protection laboratory for both for emergency and routine radiation monitoring.

Materials and methods

Two procedures developed by the International Atomic Energy Agency were chosen for the present study, as follows: "IAEA/AQ/12 - A Procedure for the Determination of ^{210}Po in Water Samples by Alpha Spectrometry" [1], and "IAEA /AQ/34 - A Procedure for the Sequential Determination of Radionuclides in Phosphogypsum Liquid Scintillation Counting and Alpha Spectrometry for Po^{210}, Pb^{210}, Ra^{226}, Th and U radioisotopes" [2]. These procedures are generally applicable and need to be adapted according to the laboratory's specific conditions, equipment and materials available.

The analytical method involves the following major steps:
- Sample collection;
- Sample preparation;
- Chemical separation and purification of the Po in order to avoid interference from other natural or artificial α-emitting radionuclides and stable elements in the test sample;
- Source preparation by spontaneous deposition of Po on a silver disk;
- Measurement by alpha spectrometry;
- Calculation of analytical result and combined uncertainty.

The paper focuses on the sample collection and preparation stages of the analytical procedure, since represent the most sensitive part of the measurement procedure.

Sample collection

The time interval between sample collection and analysis should be kept as short as possible. In environmental samples, the Po^{210} is not always in equilibrium with its Pb^{210} parent. If the initial activity of Pb^{210} is much higher than the Po^{210} activity, or the time period between sampling and Po separation is long, the Po^{210} activity changes considerably from its initial value at the sampling date due to the production of Po^{210} from the Pb^{210} decay and the decay of the Po^{210} itself. This has to be considered in the calculation of decay correction of the Po^{210} activity to the sampling date (see Fig. 1) [3]. The uncertainty of Po^{210} calculated to the sampling date can be more significantly affected by the time interval between the separation date and the sampling date in comparison with that of Pb^{210}, due to the short half life of Po^{210} [3].

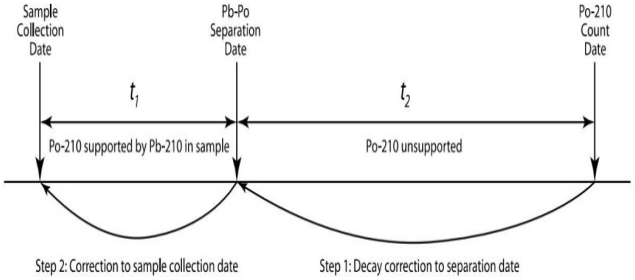


Fig. 1. Decay and ingrowth corrections for Po^{210} determination, considering the time intervals t_1 (separation date − sampling date) and t_2 (count date − separation date), [3]

Sample preparation

Sample preparation methods are applied depending on the type of matrix and the amount of sample used. A very important aspect during sample preparation is the temperature control, which prevents polonium from volatilizing at high temperatures and resulting in a significantly reduced radiochemical yield. Relevant studies have shown that various polonium compounds begin to volatilize at 100 ºC, and when the temperature reaches 300 ºC, 90% of the polonium can completely evaporate. Chlorides, organic compounds, and chelates of polonium are particularly volatile, and all polonium complexes volatilize below 200 ºC. As a result, temperature control is essential during the environmental samples pretreatment.

To determine the natural content of Po^{210} in water samples, large sample volume need to be processed, considering the very low levels of its concentration. Evaporating the entire amount of water, in order to concentrate the radionuclides, is not a viable option in this case, being time and energy consuming. That is why the co-precipitation procedure with MnO_2 was used, in order to preconcentrate Po^{210} from aqueous samples.

Solid sample preparation comprises both physical and chemical techniques involving drying, grinding and sieving, and extraction of Po^{210} for the sample matrix. Chemical preparation involves dissolution of the sample and organic matter destruction. Microwave digestion method offers digestion and decomposition of both inorganic and organic matrices associated, under controlled conditions. The advantages of the microwave digestion method are the following: time saving, simultaneous processing of several samples, acid consumption lower in microwave digestion, higher extraction efficiency, and reduced exposure of the analyst to corrosive acid vapors.

For the experimental tests performed in this study, it was used a Speedwave Xpert Berghof microwave oven. The digestion program used to minimize polonium losses is presented in the table below.

Table 1. Digestion program for decomposition of samples with polonium content

Step	T [°C]	P [bar]	Ta [min]	Time [min]	Power [%]
1	60	10	5	5	30
2	90	20	10	50	45
3	50	0	0	0	0
4	50	0	0	0	0

The digested samples were visually inspected. In several soil samples, presence of undissolved silica was noticed. In these cases, the sample was centrifuged, the residue was transferred back to the reaction vessel and the mixture of specific acids was added. The dish was placed in the microwave digester under the same conditions as above. The stages in solid samples processing by microwave digestion are illustrated in Fig. 2.



Fig. 2. Samples processing by microwave digestion

Chemical separation of polonium is carried out by Sr-resin extraction chromatography. The chemical separation step improves the reliability of the procedure in terms of both recovery and spectrum peak resolution by removing interfering elements present in the sample. The date of separation must be recorded, as it represents the date of isolation of Po^{210} from its parents Pb^{210} and Bi^{210}.

The most commonly used form of source preparation for determination of Po^{210} by alpha spectrometry is the spontaneous deposition on silver discs (see Fig. 3), as it is simple and ensures separation of polonium from other alpha-emitting radionuclides and matrix elements which may not have been completely separated in the chemical separation step. The spontaneous deposition of Po is also possible onto disks of copper, stainless steel, or nickel, but deposition efficiency drop by about 7-8%, under the same conditions.



Fig. 3. Chemical separation and spontaneous deposition on silver discs

Alpha spectrometry is an optimal method for the determination of Po^{210} content in environmental samples. The main principle of this method is to add an isotopic tracer of known activity in the soil sample. The most widely used tracers for the determination of Po^{210} are Po^{208} and Po^{209}, respectively. However, ^{209}Po is more used than Po^{208} due to seeral reasons: better energy resolution and easier deconvolution of alpha spectra, the half-life of Po^{209} allows to be used more years in the laboratory, Po^{208} solutions may contain Po^{209} tracer (as shown in Fig. 4).

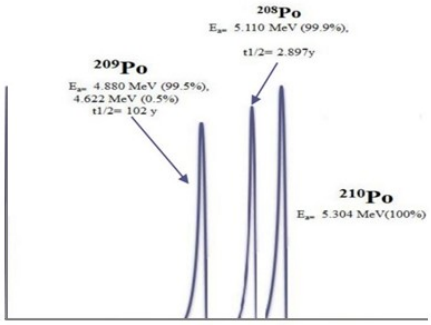


Fig. 4. Spectrum for Po^{209} and Po^{210} tracers

Fig. 5 presents an example of the spectrum obtained during the measurement of soil sample IAEA 448. The separation was efficient, as evidenced in the spectrum by the presence of the Po^{209} tracer peak at 4883.0 keV energy and the Po^{210} peak at 5304.38 keV energy.

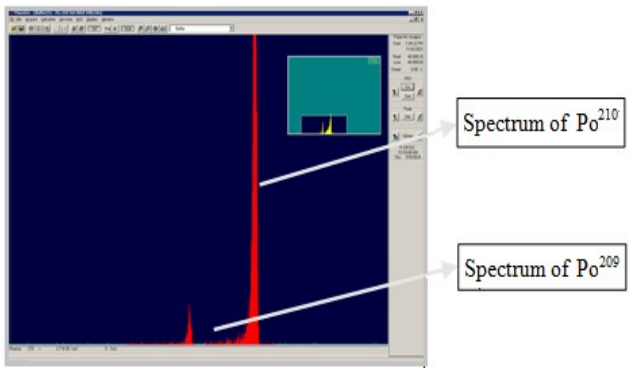


Fig. 5. Spectrum for Po^{209} and Po^{210} tracers Reference Material _Soil IAEA 448

Results and discussion

For the simulation of contaminated environmental samples, the following samples were used: spiked water and fish samples provided within the IAEA_ALMERA (Analytical Laboratories for the Measurement of Environmental Radioactivity) proficiency tests with known Po^{210} activity concentration [4-6], a reference material soil, IAEA 448, with known Ra^{226} activity concentration [7], and a reference material phosphogypsum, IAEA 434, with known Pb^{210} activity concentration [8].

The samples' identification is given in Table 2. To evaluate the recovery yield, Po^{209} was used as an alpha-emitting radioactive tracer.

Table 2. Samples' ID

Sample	ID
Dried fish spiked with anthropogenic and natural radionuclides (ALMERA 2020, [4])	S1
Spiked water, anthropogenic and natural radionuclides, gross α and β (ALMERA 2022, [5])	S2
Spiked water, anthropogenic and natural radionuclides including H^3, Sr^{90} and gross α and β (environ. levels) (ALMERA 2022, [5])	S3
Spiked water, anthropogenic and natural radionuclides including Sr^{90}, Ra^{226} and progeny (ALMERA 2023, [6])	S4
Soil Reference material IAEA 448, [7]	S5
Phosphogypsum Reference material IAEA 434, [8]	S6.1
	S6.2

The radioanalytical method final results were obtained from the alpha spectra generated by measuring with a passive implanted silicon detector (PIPS). In order to be able to determine activity concentration of Po^{210} in samples, other parameters were used, such as the mass of the sample, the amount of tracer added, the recovery yield of the tracer.

The results for S1-S4 samples were evaluated under the interlaboratory comparison/proficiency tests conducted by the IAEA ALMERA Network in 2020, 2022 and 2023.

A number of radiation protection laboratories from the IAEA ALMERA Network encountered difficulties in obtaining reliable results on Po^{210} determination in the provided samples, as can be seen in Figs. 6 – 9.

The values reported by the RATEN ICN' Laboratory have been accepted in terms of precision and accuracy, and are given in Table 3. The charts containing the results reported for the S1, S2, S3 and S4 samples, with the percentage of accepted and not accepted values, are shown in Fig. 6.

In Figs. 7 – 9, the Po^{210} activity concentration is illustrated for the reported results under IAEA ALMERA proficiency tests 2020, 2022 and 2023, respectively. The values reported by the RATEN ICN's laboratory are marked on the graphs using a blue rectangle.

The results of ^{210}Po activity concentrations obtained for the reference material soil - IAEA 448 (S5 sample) and phosphogypsum - IAEA 434 (two replies S6.1 and S6.2 samples) are presented in Table 4.

The discrepancies between the determined values of the Po^{210} activity concentration and the certified values are shown in Fig.10.

Table 3. Results of RATEN ICN on Po^{210} determined in the fish and spiked water samples, IAEA_ALMERA proficiency test [4 – 6]

Sample ID	Reference value (Bq/kg)	Determined value (Bq/kg)	Bias (%)	Z-score	Accuracy	Precision	Final Score	Recovery yield (%)	Minimum detectable activity concentration (Bq/kg)
S1	97.4	90.9	-6.67	0.09	A	A	A	52.4	1.9
S2	31.6	33.18	5.00	0.83	A	A	A	15.5	0.14
S3	5.29	3.92	-25.90	4.28	A	A	A	16.5	0.08
S4	5.21	6.56	25.91		A	A	A	61.7	0.02

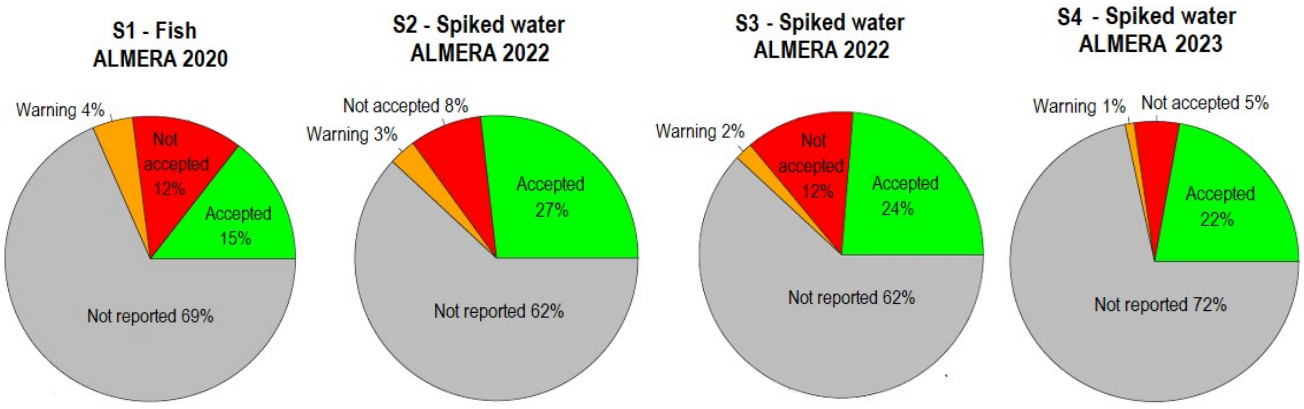


Fig. 6. Chart with percentage of accepted, warnings, not accepted and not reported results for Po^{210} determination in fish and spiked water samples provided for the IAEA_ALMERA proficiency tests [4-6]

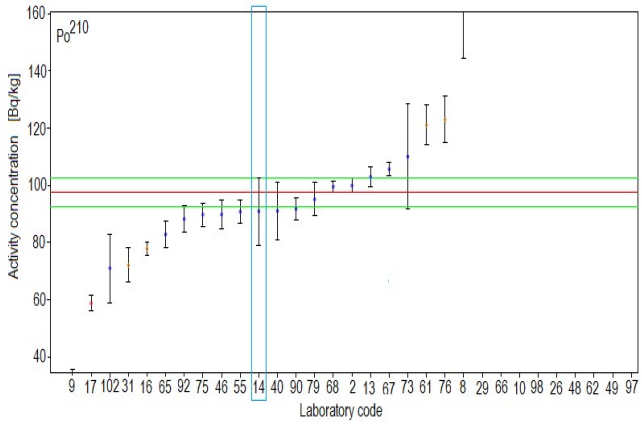


Fig. 7. Reported Po^{210} activity concentration for sample S1, IAEA_ALMERA 2020 proficiency tests [4] RATEN ICN Laboratory's ID = 14

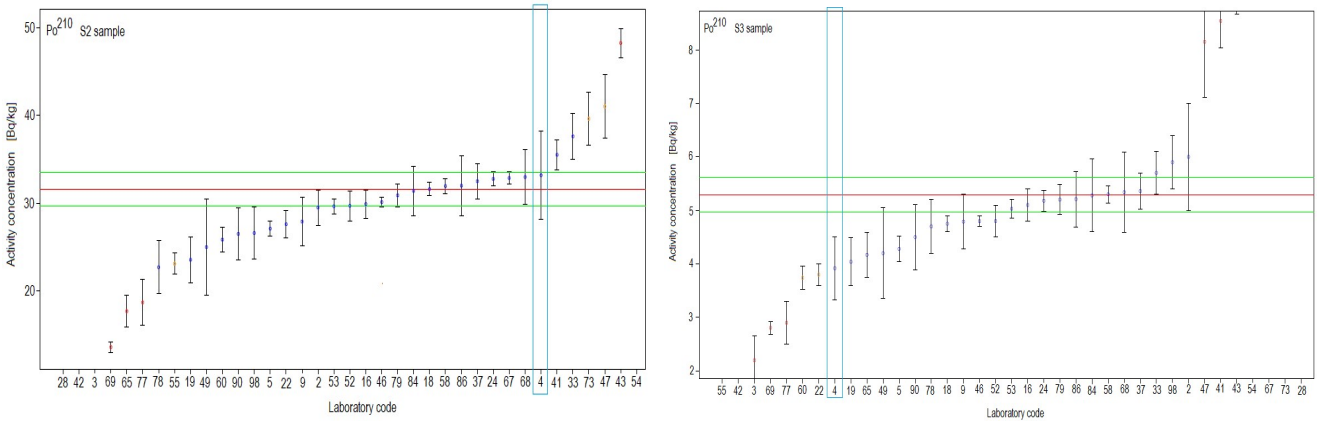


Fig. 8. Reported Po^{210} activity concentration for samples S2 (left) and S3 (right), IAEA_ALMERA 2022 proficiency tests [5]
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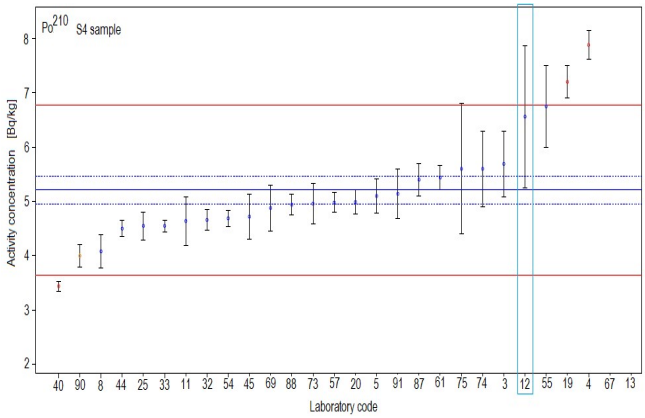


Fig. 9. Reported Po^{210} activity concentration for sample S4, IAEA_ALMERA 2023 proficiency tests [6]
RATEN ICN Laboratory's ID = 12

Table 4. Results of RATEN ICN on Po^{210} determined in the soil (S5, IAEA 448) and phosphogypsum (S6.1 and S6.2, IAEA 434) samples, [7, 8]

Sample ID	Certified value (Bq/kg)	Determined value (Bq/kg)	Discrepancy (%)	Recovery yield (%)	Minimum detectable activity concentration (Bq/kg)
S5	10110	11010	8.9	32.6	0.01
S6.1	409.26	381.31	6.8	40.4	5.37
S6.2	409.26	400.95	2.03	29.6	6.96

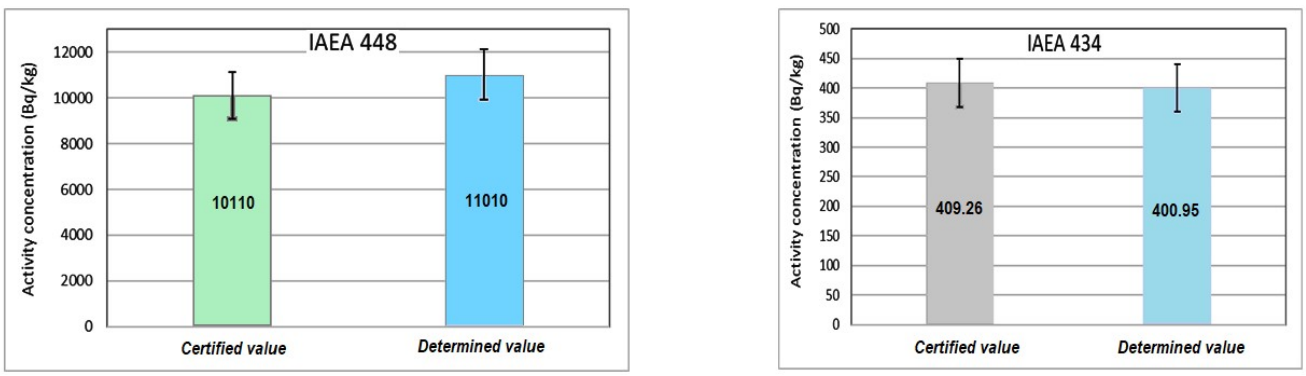


Fig.10. Discrepancy between Certified Value and Determined Value for Reference Materials, Soil (IAEA 448) and Phosphogypsum (IAEA 434)

Conclusions

The paper presented several results of experimental tests carried out for the selection and implementation of appropriate radioanalytical methods to determine the content of Po^{210} in environmental samples.

The sample processing technique was based on the separation of Po^{210} by resin extraction for strontium. The preparation of the counting sources was achieved by spontaneous deposition on silver discs.

In order to simulate tests on some contaminated samples, with known Po^{210} activity, certified reference materials were used, as follows: some samples provided by IAEA ALMERA Network for proficiency tests, and IAEA reference materials. The measured samples covered a relatively wide range of Po^{210} activity concentration values and a varied range of matrices (spiked water, fish, soil, phosphogypsum).

The discrepancies of the results obtained by the RATEN ICN Radiation protection Laboratory, in relation to the certified values of the Po^{210} activity concentration, were within the estimated uncertainty limit.

In conclusion, the radioanalytical method used in the paper can be implemented in the monitoring of environmental radioactivity.

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