RAPID DETERMINATION OF ^{210}Po AND ^{210}Pb (VIA ^{210}Bi) IN AIR FILTERS USING ALPHA SPECTROMETRY AND CERENKOV COUNTING

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ABSTRACT. The paper describes a routine analytical method for the separation and quantification of ^{210}Po and ^{210}Pb from air filters used in the ground level atmospheric sampling stations throughout the United Kingdom. A sample of air filter material is dissolved in fuming nitric acid and the ^{210}Po is separated from lead radioisotopes by co-precipitation on manganese dioxide. The ^{210}Po is autodeposited on to a silver disc and counted by alpha spectrometry. The supernatant containing the ^{210}Pb is separated from ^{210}Bi and ^{210}Po daughter products by anion-exchange chromatography using hydrobromic and hydrochloric acids. The ^{210}Bi daughter is then allowed to grow-in to secular equilibrium with the ^{210}Pb parent and quantified by Cerenkov counting. Determination of the ^{210}Pb via Cerenkov measurement of the ^{210}Bi daughter avoids the need to leave samples for prolonged periods before measuring ingrown ^{210}Po, whilst still achieving sufficiently low limits of detection to permit quantification of ^{210}Pb in air filter materials. This rapid analytical method has been accredited by the United Kingdom Accreditation Service and is used routinely for the analysis of the monthly air filter samples from the environmental monitoring program.

INTRODUCTION

Uranium and thorium occur naturally in all rocks. Certain rocks, such as monazite under the North Sea, contain relatively high concentrations. Decay of these naturally occurring radioactive materials (known as NORM) produces series of other radioactive materials, some of which form gases such as radon, before reforming as solids. The sintering processes at steel works, which involve the fusing of various iron ore fluxes, gives rise to post combustion gases that are emitted to the atmosphere. These gases can contain lead and polonium. Polonium and lead can be concentrated through uptake in flora and fauna such as blackberries and calf liver, and, hence, can enter the food chain.

A program for the routine monitoring of radioactivity in air and rainwater was established in the United Kingdom (UK) in the 1950s and is managed currently by the Environment Agency (the Agency) on behalf of the Department of the Environment, Food, and Rural Affairs (DEFRA). This program forms part of the UK Government's arrangements for meeting its obligations under Article 35 of the EURATOM Treaty to monitor radioactivity in air, soil, and water. The contract to carry out this work was awarded by competitive tendering to NNC Limited in November 1998, and so the Winfrith Environmental Level Laboratory (WELL) was established in December 1998 at the Winfrith Technology Centre in Dorset, UK.

The Agency is interested in monitoring for these nuclides in particular for dose assessment purposes—^{210}Po having a high dose coefficient and being naturally produced and supported. This paper concentrates on the analysis of just two of the radiologically important nuclides—^{210}Po and ^{210}Pb.

Airborne particulate material is sampled continuously at about one metre above ground level at a sampling station in Chilton, Oxfordshire (latitude 51½ °N, longitude 01½ °W). The air is passed through filters made of polyester fiber at a rate of 10,000 kg per day. The efficiency of the filter material has been measured at greater than 95% for particles of 0.3 µm aerodynamic diameter at the flowrates used. These filters are changed each week, and every fourth week a 10% by area sub-sample is taken and returned to the WELL on the same day for analysis. Analysis of these sample types should always be within one week of sub-sampling to minimize the effect of ingrowth of ^{210}Po from

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the ^{210}Pb present in the sample, and minimize the losses by decay of any unsupported ^{210}Po. There are several radiochemical methods documented for ^{210}Pb and ^{210}Po determination. One routine method for the determination of the ^{210}Pb content of the sample involves separating the ^{210}Pb from the ^{210}Po, and then allowing the ^{210}Po to grow-in over a period of at least three months. The resulting ^{210}Po would then be quantified by alpha spectrometry, and the activity of the ^{210}Pb could then be calculated mathematically. A sufficiently long grow-in time is required to minimize uncertainties and improve limits of detection.

An alternative analytical method for quantifying the ^{210}Pb involves separating the ^{210}Pb from the ^{210}Bi and ^{210}Po daughters, and allowing the ^{210}Bi daughter to grow-in to secular equilibrium with the ^{210}Pb parent over a one-month period. The ^{210}Bi is then quantified by Cerenkov counting. Determination of the ^{210}Pb via Cerenkov measurement of the ^{210}Bi daughter avoids the need to leave samples for prolonged periods before measuring ingrown ^{210}Po, whilst still achieving sufficiently low limits of detection to permit quantification of ^{210}Pb in air filter materials. This rapid analytical method has been accredited by the United Kingdom Accreditation Service and is used routinely for the analysis of the monthly air filter samples from the environmental monitoring program, and is described in this paper.

METHODOLOGY

Reagents

All reagents used were of analytical grade, and prepared with deionized water as applicable. Acetone, methanol, hydrochloric and nitric acids were supplied by Merck Ltd., Lutterworth, Leicester, UK. Anion exchange resin (Dowex® 1X8–200, quaternary amine type, strong base, 100–200 mesh, 8% cross linked, chloride form), and all other reagents were supplied by Aldrich Chemical Company Ltd., Gillingham, Dorset, UK. ^{210}Pb was supplied as lead and bismuth nitrates in solution (37.6 ± 1.1 kBq/g) by Isotrak, AEA Technology QSA, Harwell, Oxfordshire, UK. ^{209}Po was supplied carrier free in nitric acid solution (5.043 ± 0.151 Bq/g) by Isotrak as well. Each standard solution was diluted by mass to produce working solutions in the range of 750 Bq/g for ^{210}Pb and 0.253 Bq/g for ^{209}Po, and are traceable to national standards.

Analytical Separation

The air filter sub-sample for analysis is cut into small pieces and placed in a round bottomed flask. A reagent blank and lead method control standard are prepared similarly from unexposed air filter material of the same quantity (14 cm × 14 cm, ~7 g). To each sample are added 25 mg Pb, and 5 mg Bi as inactive carriers and the Pb yield monitor. The reagent blank and sample are both spiked with ^{209}Po (0.253 Bq) as a yield monitor, and the lead method control standard is spiked with ^{210}Pb (750 Bq). All samples are analyzed as follows:

The sample is wet oxidized, under reflux, with fuming nitric acid (99.5%) until the filter material has been dissolved, and then allowed to cool to room temperature. The liquor is transferred to a beaker, and diluted to 300 mL with deionized water prior to filtration through a Whatman No. 542 filter paper. The filtrate is heated on a hotplate, and evaporated to 200–250 mL, then allowed to cool to room temperature. A solution of 10% ^{w}/v potassium permanganate is added until precipitation of manganese dioxide is complete. Polonium radioisotopes are co-precipitated with the manganese dioxide in the acidic medium, and the ^{210}Pb remains in solution. The date and time of the separation is recorded for decay correction calculations. The manganese dioxide precipitate is filtered through

a 0.8 μm membrane filter, and reserved for the Po analysis (the precipitate from the lead method control standard can be discarded). The filtrate is reserved for the Pb analysis.

Polonium Analysis

The manganese dioxide precipitate is dissolved in the minimum volume of a solution of hydrogen peroxide in 3M hydrochloric acid (2 mL 30% $^{w}/_{v}$ hydrogen peroxide + 98 mL 3M hydrochloric acid). The solution is made up to 40 mL with deionized water, and boiled gently on a hotplate for at least 10 min to decompose the excess hydrogen peroxide. Ascorbic acid (0.5 g) is added to ensure any ferric ions present are reduced to the +2 oxidation state, and do not interfere with the autodeposition of the Po on to the Ag discs.

Silver discs of 27 mm diameter are prepared, prior to autodeposition, by covering one side with strong tape, and polishing the surface to be plated with household silver polish. The disc is then mounted vertically in a slit cut into a PTFE support block, and placed in a 50 mL beaker. The solution is transferred to the beaker, and deionized water is added to ensure that the disc is immersed. The top of the beaker is covered with labfilm, and secured with an elastic band. The beaker and contents are heated in a thermostatically controlled water bath set at 60 °C, and the Po allowed to autoplate on to the silver disc for at least overnight. The beaker is removed from the water bath, and the Ag disc retrieved. The disc is washed with deionized water, and the backing tape removed. The disc is washed with acetone and then methanol, and allowed to air dry. The disc is counted by alpha spectrometry using a Harwell Instruments Ltd. (Canberra) Alpha Analyst system.

Lead Analysis

The filtrate from the manganese dioxide separation, containing the Pb, is transferred to a beaker, and evaporated to dryness on a hotplate. The residue is dissolved in 50 mL concentrated nitric acid, evaporated to dryness again, and this step is repeated. The residue is dissolved in 50 mL 1:1 hydrobromic acid solution (i.e. 25 mL 48% hydrobromic acid + 25 mL deionized water), and evaporated to dryness to metathesise the lead to the bromide form. The residue is dissolved in 100 mL 1:49 hydrobromic acid solution (i.e. 2 mL 48% hydrobromic acid + 98 mL deionized water) prior to separation by anion exchange chromatography.

A 1 cm × 20 cm chromatography column is prepared by slurrying the anion exchange resin with 1:1 hydrobromic acid solution, and transferring to the column to a resin depth of 9 cm. The resin is conditioned by washing first with 25 mL 1:1 hydrobromic acid solution, and then with 50 mL 1:49 hydrobromic acid solution. The sample solution is passed through the column at the maximum flow rate under gravity, which retains the Pb on the resin. The resin is washed with a further 50 mL 1:49 hydrobromic acid solution, and all washings are discarded. The Pb is eluted into a clean beaker with 50 mL 6M hydrochloric acid. The eluate is heated on a hotplate, and evaporated to 25 mL, then allowed to cool to room temperature. Concentrated sulphuric acid is added dropwise until precipitation of lead sulphate is complete. The date and time of the precipitation is recorded to determine the date when the ^{210}Bi has grown into secular equilibrium. The sample is centrifuged and the supernatant discarded. The precipitate is washed with 20 mL deionized water, centrifuged, and the washings discarded. The precipitate is transferred to a clean, pre-weighed 22 mL glass scintillation vial with a small volume of absolute ethanol. The ethanol is evaporated to dryness under an infrared lamp, and the vial is allowed to cool to room temperature. The vial and precipitate are re-weighed to calculate the weight of lead sulphate recovered as the yield monitor. The precipitate is dissolved in 10 mL 6M hydrochloric acid, the vial capped, and set aside for at least 33 days from the date of the lead sulphate

precipitation to allow the ^{210}Bi to grow-in to secular equilibrium. The vials can then be counted by Cerenkov counting using a Packard 2250CA® liquid scintillation analyzer.

Sample Counting

The silver disc with the autoplated ^{210}Po and ^{209}Po internal standard is counted by alpha spectrometry using a multi-chamber Harwell Instruments Ltd. (Canberra) Alpha Analyst system. Each detector is a passivated implanted planar silicon (PIPS), model number A450–18AM, and has a counting efficiency of 16.4–16.6% at the standard geometry used of a source-detector distance of 9 mm. A typical chamber background count rate is 0.5 cph over an energy range of 3.5–6.5 MeV, with an air thickness of 14 μg/cm^2 set by default for recoil suppression. The detector is energy and efficiency calibrated, and performance checked using separate mixed alpha discs traceable to national standards. The reagent blank and sample discs are counted for a week, and the FWHM for each ^{210}Po and ^{209}Po peak is 20–25 keV. No interfering radionuclide peaks are observed. Analytical results are decay corrected to the date and time of the manganese dioxide precipitation as recorded earlier. The reagent blank sample disc typically has a ^{210}Po reported activity in the range of (7–10) ± 10% mBq/disc (1σ), while the sample disc typically has a ^{210}Po reported activity in the range of (90–200) ± 5% mBq/disc (1σ). The total weight of air sampled through the sub-sample of the filter is 7900 ± 200 kg.

Cerenkov counting of the reagent blank, sample and method standard sample vials, containing the ^{210}Pb/^{210}Bi, is performed using a Packard 2250CA® liquid scintillation analyzer in high sensitivity count mode. The samples are dark-adapted prior to counting, and the counting efficiency of the samples is determined by counting a ^{210}Pb reference standard solution prepared as per the analytical samples. The protocol that is set up counts each vial twice for 200 min, over an energy window of 0–20 keV. The reagent blank sample is typically 18–19 cpm using high performance glass vials, with the counting efficiencies in the range 14–16%. The net sample count rate is typically in the range of (0.06–0.20) ± 0.01 cps (1σ). Analytical results are decay corrected to the mid-point of the sampling period as applicable. Again, the total weight of air sampled through the sub-sample of the filter is 7900 ± 200 kg. From these results, correction factors can then be applied to the calculated ^{210}Po results for the ingrowth of ^{210}Po from the ^{210}Pb present in the sample.

Cerenkov counting has many advantages over conventional liquid scintillation counting. Radionuclides need to have β-decay energies greater than a few hundred keV to be detected and as a result many radionuclides do not interfere with the ^{210}Bi measurement even if they are co-precipitated with the lead sulphate prior to dissolution in the vial. Chemical quenching is not observed in Cerenkov counting and the counting efficiencies are not reduced through color quenching in colored samples. The lead sulphate precipitate is dissolved in 6M hydrochloric acid, and because a liquid scintillant is not being used the whole sample can be counted and is not affected by the acid concentration. The sample is easily recoverable following the Cerenkov measurement if further analysis is required.

DISCUSSION

The main requirement for the separation and analysis scheme of the air filter sample is that it should allow rapid and quantitative determination of the ^{210}Pb and ^{210}Po, while still achieving sufficiently low limits of detection to permit quantification of these radioisotopes in this matrix. The time taken from receipt of air filter sample to counting source preparation is four person-days, prior to the grow-in being completed for the ^{210}Bi. Statistical analysis of the data collected over a two-year period for the individual method control reference standard solutions has enabled the following overall method uncertainties, precision, and accuracy values to be calculated:

- ^{210}Pb method control sample with a total of n = 27 individual analyses, which include single samples, and batch samples for repeatability studies.
- Mean ^{210}Pb % method efficiency = 99.06 ± 7.10 (1σ)
- ^{209}Po internal standard with a total of n = 46 individual analyses, which include single samples, and batch samples for repeatability studies.
- Mean ^{209}Po % method recovery = 20.68 ± 7.27 (1σ)

The yield determination for the ^{210}Pb analysis is by the addition of an aliquot of lead carrier, and then weighing the final precipitate of lead sulphate. The lead carrier is prepared by dissolving 10.0000 ± 0.1000 g lead nitrate in deionized water with concentrated nitric acid, and making up to volume in a calibrated, 250 mL Class A volumetric flask. One milliliter of carrier is added which would give, theoretically, a 100% recovery of 36–37 mg lead sulphate, depending on the exact reagent weight and flask volume. Typical recoveries of the final lead sulphate precipitate are in the range of 18–28 mg, and this allows a measurable quantitative weight. The anion exchange resin used (Dowex® 1X8–200, quaternary amine type, strong base, 100–200 mesh, 8% cross linked, chloride form) in hydrobromic and hydrochloric acid media provides a highly selective way of separating the ^{210}Pb from its daughter products. Literature values (Korkisch 1989) for the distribution coefficients of Pb, Bi and Po on this resin show that Pb is quantitatively removed in 6M hydrochloric acid, while Bi and Po are retained. It also shows a quantitative adsorption of Pb and Bi from low concentrations of hydrobromic acid. No data are given though for Po adsorption from hydrobromic acid, and so experiments were conducted to determine these distribution coefficients. Approximately 4 Bq of ^{209}Po were spiked into 10 mL hydrobromic acid with concentrations ranging from 0.3–3 M. 0.05 g of Eichrom 1X8 100–200 mesh anion exchange resin was added to each vial and the mixture shaken for 1 hr. The mixture was filtered through a 0.45 μm membrane filter and the activity of ^{209}Po was determined in an aliquot of the filtrate using liquid scintillation counting. The distribution coefficient for Po on anion exchange resin for all hydrobromic acid concentrations was greater than 5000. As can be seen from the % method efficiency data of the ^{210}Pb control standard, the precision and accuracy obtained by Cerenkov counting of the ^{210}Bi daughter is quantitative, as well as being rapid enough for the data to be reported in a timely fashion. Analytical results of the sample counting from the reagent blank and air filter sub-sample show that the method is applicable to the measurement of the low levels of ^{210}Pb in the atmosphere at the site of the sampling station.

The yield determinand for the ^{210}Po analysis is the internal ^{209}Po tracer. Data obtained from the % method recovery of the ^{209}Po tracer show that the precision and accuracy is much lower than for the ^{210}Pb analysis. Separation of the Po radioisotopes from the ^{210}Pb in the air filter, by co-precipitation with manganese dioxide, is achieved quickly, which minimizes the effect of ingrowth of ^{210}Po from the ^{210}Pb present in the sample and losses by decay of any unsupported ^{210}Po. Despite the lower precision and accuracy, analytical results of the sample counting from the reagent blank and air filter sub-sample show that the method is applicable to the measurement of the low levels of ^{210}Po in the atmosphere at the site of the sampling station. Improvements to the recovery of the Po radioisotopes will be investigated, and there is literature available for the optimization of the final autoplating step (Flynn 1968).

The results for 1999 (Dale 1999) of the measured ^{210}Po and ^{210}Pb concentrations in the air at the sampling station are shown in Figure 1 and Table 1.

The calculated individual radioisotope radioactivity concentrations (Bqkg^{-1}) and the ^{210}Po to ^{210}Pb ratio of 0.13 are consistent with literature values obtained for surface air (Arnand and Rangarajan

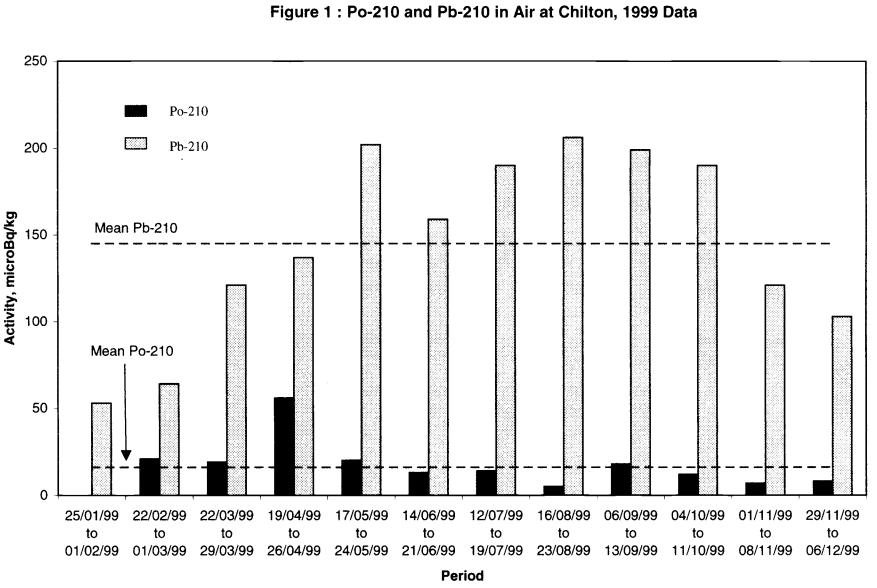

Figure 1 Po-210 and Pb-210 in air at Chilton; 1999 data.

Table 1 Four weekly Chilton ^{210}Po and ^{210}Pb results for 1999

Period from	Period to	^{210}Po (μBqkg^{-1})	^{210}Pb (μBqkg^{-1})	$\frac{^{210}Po}{^{210}Pb}$
25-Jan-99	01-Feb-99	ND	53 ± 22	NA
22-Feb-99	01-Mar-99	21 ± 5	64 ± 36	0.33
22-Mar-99	29-Mar-99	19 ± 2	121 ± 31	0.16
19-Apr-99	26-Apr-99	56 ± 6	137 ± 67	0.41
17-May-99	24-May-99	20 ± 2	202 ± 17	0.10
14-Jun-99	21-Jun-99	13 ± 2	159 ± 28	0.08
12-Jul-99	19-Jul-99	14 ± 2	190 ± 26	0.07
16-Aug-99	23-Aug-99	5 ± 2	206 ± 45	0.02
6-Sep-99	13-Sep-99	18 ± 2	199 ± 23	0.09
4-Oct-99	11-Oct-99	12 ± 2	190 ± 20	0.06
1-Nov-99	8-Nov-99	7 ± 2	121 ± 40	0.06
29-Nov-99	6-Dec-99	8 ± 2	103 ± 41	0.08
Annual means		16 ± 1	145 ± 10	0.13

1990; Paatero and Hatakka 1997; Carvalho 1995; Hussain et al. 1990). Results are reported with an estimate of counting uncertainty at the 95% confidence level (1.96 σ).

CONCLUSIONS

The determination of ^{210}Po, and subsequent quantification of ^{210}Pb by Cerenkov counting of the ^{210}Bi daughter, has reduced the analysis time required to achieve satisfactory results for the separa-

tion and analysis of air filter samples, with sufficiently low limits of detection for the matrix. The time taken from receipt of air filter sample to counting source preparation is four person-days, prior to the grow-in time of 33 days for the ^{210}Bi. Statistical analysis of the data collected over a two-year period for the individual method control reference standard solutions has provided the overall method uncertainties, precision and accuracy values, and this rapid analytical method has been accredited by the United Kingdom Accreditation Service.

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