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Quantitation of lead-210 (^{210}Pb) using lead-203 (^{203}Pb) as a “Massless” yield tracer

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Abstract

Determination of Pb-210 (^{210}Pb) in aqueous solution is a common radioanalytical challenge in environmental science. Widely used methods for undertaking these analyses (*e.g.*, ASTM D7535) rely on the use of stable lead (Pb) as a yield tracer that takes into account losses of ^{210}Pb that inevitably occur during elemental/radiochemical separations of the procedures. Although effective, these methods introduce technical challenges that can be difficult to track and potentially introduce uncertainty that can be difficult to quantify. Examples of these challenges include interference from endogenous stable Pb in complex sample matrices; contamination of stable Pb carrier with ^{210}Pb ; and high detection limits due to counting efficiency limitations. We hypothesized that many of these challenges could be avoided by the use of the electron-capture, gamma-emitting isotope, ^{203}Pb as a chemical yield tracer in the analysis of ^{210}Pb .

A series of experiments were performed to evaluate the efficacy of ^{203}Pb as a tracer. Four different matrices were analyzed, including a complex matrix (hydraulic-fracturing produced fluids); and samples comprising less complicated matrices (*i.e.*, river water, deionized water, and tap water). Separation techniques and counting methodologies were also compared and optimized. Due to a relatively shorthalf life (52 h), ^{203}Pb tracer is effectively massless for the purposes of chemical separations, allowing for reduced chromatography column resin bed volumes. Because ^{203}Pb is a gamma emitter (279 keV; 81% intensity), recovery can be determined non-destructively in a variety of matrices, including liquid scintillation cocktail. The use of liquid scintillation as a counting methodology allowed for determination of ^{210}Pb activities via ^{210}Pb or ^{210}Po ; and recoveries of greater than 90% are routinely achievable using this approach. The improved method for the analysis of ^{210}Pb in aqueous matrices allows for the analysis of complex matrices, at reduced cost, while providing greater counting flexibility in achieving acceptable detections limits.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvrad.2017.02.003>.

Keywords

Lead-210; Polonium-210; Lead-203

1. Introduction

Lead-210 (^{210}Pb) is a naturally-occurring radionuclide in the uranium-238 (^{238}U) decay series. ^{210}Pb analysis has been used as a natural tracer for describing natural phenomenon (*e.g.*, sedimentation rates) (Appleby and Oldfield, 1978; Nittrouer et al., 1979; Robbins and Edgington, 1975). The environmental impacts of anthropogenically-enhanced naturally-occurring ^{210}Pb and its direct decay product polonium-210 (^{210}Po) are also under investigation (Eitrheim et al., 2016; Nelson et al., 2015; Seiler and Wiemels, 2012; Vengosh et al., 2014). ^{210}Pb is perhaps one of the most challenging radionuclides to quantitate in the ^{238}U decay series. Complicating factors include: (1) its moderate-half life ($t_{1/2} = 22.2$ years), which results in masses of ^{210}Pb too low for quantitation on most mass spectrometry systems; (2) a weak, low abundant gamma-emission (46.539 keV, 4.25%), which is below the energy threshold of many gamma spectrometry systems (and requires a careful correction for sample matrix density); (3) a weak beta emission (4.6–17.0 keV, 84%, 16.16–63.5 keV, 16%); and (4) a lack of a short-lived gamma-emitting progeny that would allow for non-destructive quantification based on daughter ingrowth (NNDC (National Nuclear Data Center), 2014). Consequently, most methods designed to quantitate ^{210}Pb rely on chemical separations where (1) chemical recoveries are determined by relatively large quantities (10 mg or more) of stable Pb, and (2) activities are determined by beta emissions from the ^{210}Pb progeny, bismuth-210 (^{210}Bi).

A widely used exemplary method for the determination of ^{210}Pb concentration in water is ASTM D7535. In brief, this method calls for the addition of stable Pb (10 mg, used to determine overall chemical yield) to the aqueous sample. A ferric hydroxide (FeOH_3) co-precipitation is then used to concentrate Pb and ^{210}Pb from the bulk solution. The FeOH_3/Pb precipitate is dissolved in nitric acid (HNO_3) and the Pb is selectively adsorbed to a 2-mL Pb-specific chromatography resin-bed column (Pb-Resin; Eichrom Technologies). As written, the methods calls for elution of Pb from the column using deionized water, followed by precipitation as lead sulfate (PbSO_4), which is transferred to a planchet. After drying, the mass of PbSO_4 is measured and used to determine the chemical recovery of Pb and ^{210}Pb . The planchet with PbSO_4 precipitate is then held for a minimum of 5 days to allow for ingrowth of ^{210}Bi and counted via gas-flow proportional counting (GPC).

Although ASTM D7535 is effective for simple aqueous matrices (*e.g.*, drinking water), there are some technical challenges introduced by this method (and other methods relying on gravimetric determinations of Pb recovery after chemical separations). The use of stable Pb as an indicator of yield restricts the method applicability to low-endogenous-stable-Pb-containing matrices, as endogenous Pb contained in the sample can create a positive bias in the chemical yield. Since activities are divided by the yield, a higher-than-expected yield would unintentionally lower the calculated activity of ^{210}Pb . The stable Pb carrier itself also presents problems, as all Pb nitrate reagents contain small amounts of ^{210}Pb . As a result, all

Pb carrier solutions must be analyzed for ^{210}Pb prior to use and all analyses must be corrected for this contamination. These quality control and quality assurance measures increase labor and analytical expense, and introduces an additional source of uncertainty that must be included in uncertainty propagation, leading to larger relative uncertainties and increased minimum detectable activities (MDAs). The use of mass-based yield determinations also introduces uncertainty related to moisture control. The easiest way to reduce bias from moisture is to immediately count the planchet after drying; however, heat is known to interfere with the analytical balance settling. Lastly, the use of mass-based chemical yields limits the counting methodology to GPC, as the final preparation of the sample must be a dry-solid material to be weighed accurately. Other technologies with greater counting efficiencies, such as liquid scintillation counting (LSC), cannot be easily employed as the final sample preparation must generally be in a liquid form.

We sought to improve the radiochemical methodologies available for the quantitation of ^{210}Pb in a variety of environmental matrices with a wide range of complexities. We hypothesized that many of the challenges of current Pb chemical separations could be circumvented by the use of a gamma-emitting Pb isotope. One isotope that is now becoming more readily available, due to its use in the medical imaging industry, is ^{203}Pb . This isotope is a pure gamma-emitting radionuclide used as an imaging surrogate for targeted ^{212}Pb -based radionuclide therapies. It is artificially produced via proton beam irradiation of thallium (Horlock et al., 1975) and decays via electron capture, producing a number of gamma rays and x-rays, including an 80.9% abundant gamma ray at 279 keV. ^{203}Pb has a relatively short half-life of 51.92 h and as a result (at working activities) is virtually massless (NNDC (National Nuclear Data Center), 2005). We hypothesized that the radiochemical properties of ^{203}Pb would allow it to be substituted or combined with stable Pb as a radiochemical tracer for ^{210}Pb analysis. The following describes experiments using ^{203}Pb and/or stable Pb on four different aqueous matrices (hydraulic fracturing produced fluids, river water, ground-derived tap water, deionized water).

2. Material and methods

2.1. Reagents and standards

All reagents utilized in the experiments performed were ACS grade or higher. Bulk Pb Resin, 100–150 μm mesh, was purchased from Eichrom Technologies LLC. The ^{210}Pb standard used was a certified reference material (CRM A13959) purchased from the National Physical Laboratory (NPL) in the United Kingdom. ^{203}Pb radioactivity was determined by Lantheus Medical Imaging (Bellerica, MA, USA) and is based on a calibration factor derived from participation in a NIST Measurement Assurance Program. All half-lives and nuclear emission data were taken from the National Nuclear Data Center (NNDC; US Department of Energy, Brookhaven National Lab).

2.2. Instrumentation

Sample analysis was performed utilizing four different instruments. All gas-flow proportional counting (GPC) measurements were performed using a Canberra LB4200-Multi-Detector Low Background Alpha/Beta Counting System controlled by Apex-Alpha/

Beta Counting Productivity Software. Liquid scintillation counting measurements were performed using a Beckman LS6500 Liquid Scintillation Counter (LSC). Gamma measurements were performed using two high purity germanium (HPGe) gamma spectrometers (30% efficient; ORTEC, Oak Ridge, TN, USA and 18% efficient Canberra Industries, Inc., Meriden, CT, USA). Spectral acquisition, multi-channel analyzer display, energy and efficiency calibrations, and spectral analysis were conducted using ORTEC GammaVision 7 Gamma Spectroscopy Software (Env32 analysis engine).

2.3. Counting efficiency determinations

2.3.1. Gas flow proportional counting—Detectors were verified and voltage plateaus were performed in accordance with manufacturer specifications at time of installation. Briefly, an efficiency curve ranging from 3 to 12 mg of stable lead carrier was created and spiked with approximately 26 Bq of ^{210}Pb (in secular equilibrium with ^{210}Bi) directly onto each planchet. All planchets for the curve were counted in each detector and a linear regression of the data set was performed using Microsoft Excel to create a linear equation defining the counting efficiency of ^{210}Pb and ^{210}Bi in secular equilibrium versus carrier mass for each detector.

2.3.2. Liquid scintillation counting—Five glass liquid scintillation vials were prepared with 4.5 mL 0.2 M ammonium acetate and 15 mL Ultima Gold AB scintillation cocktail, spiked with 500 μL of 35.55 Bq/mL ^{210}Pb standard. A blank vial for background subtraction was also prepared with 5 mL 0.2 M ammonium acetate and 15 mL Ultima Gold AB scintillation cocktail. The efficiency vials and blank vial were counted for the same duration as the samples. Alpha/beta discrimination limits were set using ^{90}Sr and ^{230}Th , in the same aqueous solution and scintillation cocktail used for analysis. Spectrum windows of 5.0–40.0 keV for beta particles produced by ^{210}Pb and 100.0–220.0 keV for alpha particles produced by ^{210}Po were set based on observance of ^{210}Pb and ^{210}Po peaks in the liquid scintillation spectrum. Counting efficiencies were calculated as the average of individual counting efficiencies calculated for each standard vial prepared.

2.3.3. Gamma spectrometry counting—With each set of analyses, five planchets or vials were prepared by spiking the same amount of ^{203}Pb solution as was added to each of the samples, directly into the counting container. Enough ^{203}Pb was added to achieve 5000 to 10,000 net counts and the efficiency containers were counted for same duration as the samples, 3–5 min total count time. Activities for efficiencies and samples were decay corrected to the same date and time. Tracer yields were determined by dividing activity recovered in the sample (calculated from the 279.2 keV peak) by the average of the activity determined from five efficiency containers for each set. All five efficiency containers were counted on each HPGe gamma spectrometer.

2.4. Analytical Set 1—Elution with distilled water, quantitation by GPC

Three different matrices, 100 mL Marcellus-shale hydraulic fracturing produced fluid, 500 mL ground-derived tap water, and 500 mL river water, were analyzed under four separate conditions. All samples were unfiltered and adjusted to a $\text{pH} < 2$ with 16 N nitric acid at least one day prior to analysis to ensure solubilization of lead. Subset A was spiked with

^{203}Pb and 8.89 Bq ^{210}Pb ; subset B was spiked with 10 mg stable Pb carrier and 8.89 Bq ^{210}Pb ; subset C was spiked with ^{203}Pb , 8.89 Bq ^{210}Pb , and 10 mg stable Pb; and subset D was spike with 10 mg stable Pb only. The samples were then separated in accordance with ASTM D7535 methodology (key parameters 2.0 mL gravimetric Pb-Resin columns, eluted with distilled water), transferred to planchets, weighed, and counted for ^{203}Pb activity via gamma spectrometry. Stable Pb was added after separation to subset A of samples to form a PbSO_4 precipitate. Each matrix/analytical condition pair was prepared in triplicate.

2.5. Analytical Set 2—Elution with sodium citrate, quantitation by GPC

The same three matrices used in analytical set 1 were again analyzed under four separate conditions. Subset A was spiked with ^{203}Pb and 1 Bq ^{210}Pb ; subset B was spiked with 10 mg stable Pb carrier and 1 Bq ^{210}Pb ; subset C was spiked with ^{203}Pb , 1 Bq ^{210}Pb , and 10 mg stable Pb; and subset D was spike with 10 mg stable Pb only. Samples were again separated in accordance with ASTM D7535 methodology (but used 0.25 M sodium citrate as the column eluent in place of deionized water), were counted for ^{203}Pb activity via gamma spectrometry, held for three months to reach secular equilibrium (Fig. 1), and ^{210}Pb activity was determined (via the ^{210}Bi progeny) by gas flow proportional counting for approximately 1000 min. Stable Pb was added after separation to subset A of the samples to form a PbSO_4 precipitate. Each matrix/analytical condition pair was analyzed in triplicate.

2.6. Analytical Set 3—Elution with ammonium acetate, quantitation by LSC

Two different matrices, 100 mL Marcellus-shale hydraulic fracturing produced fluid and 500 mL deionized water were analyzed under two conditions (Fig. 2). Subset A was spiked with ^{203}Pb and subset B by was spiked with ^{203}Pb and 1 Bq ^{210}Pb . Samples were pre-concentrated via ferric hydroxide co-precipitation using 20 mg iron chloride carrier. The concentrate was dissolved and loaded onto 0.25 mL preconditioned Pb-Resin gravimetric columns in 2 N nitric acid. Importantly, the columns for Set 3 were much smaller than the ASTM D7535 specification of 2 mL columns. This modification was made so that elution volumes could be reduced from 20 mL to 5 mL, opening up the option direct injection into a 20 mL LSC vial with 15 mL of LSC cocktail. Pb was then eluted with 2×2.5 mL 0.2 M ammonium acetate at pH 6 into liquid scintillation vials and 15 mL Ultima Gold AB was added. Samples were counted for ^{203}Pb activity via gamma spectrometry, held for 3 weeks to allow for ^{203}Pb decay (Fig. 1), and counted for ^{210}Pb activity (via the ^{210}Pb directly and ^{210}Po progeny) for 60 min by liquid scintillation counting.

2.7. Calculations

Activity of a radionuclide (^{210}Pb , ^{210}Bi , or ^{210}Po) at the time of count was determined by equation (1):

$$A = \frac{R_G - R_B}{CF \times \epsilon \times V \times Y} \quad (1)$$

Activity at time of count was then corrected to the time of separation using equation (2):

$$A_1^0 = A_1 e^{-\lambda_1 t} \quad (2)$$

or equation (3), to convert ^{210}Po at time of count to ^{210}Pb at time of separation:

$$A_1^0 = A_3 \left(\frac{\lambda_2 - \lambda_1}{\lambda_3 \lambda_2} \right) \left(\frac{e^{-\lambda_1 t} - e^{-\lambda_3 t}}{\lambda_3 - \lambda_1} - \frac{e^{-\lambda_2 t} - e^{-\lambda_3 t}}{\lambda_3 - \lambda_2} \right)^{-1} \quad (3)$$

Where,

A = Activity, in Bq/kg

R_G = Gross count rate, in min^{-1}

R_B = Background count rate, in min^{-1}

CF = Conversion factor, 60 s min^{-1}

ε = Counting efficiency

V = Sample amount, in kg

Y = Carrier/tracer yield

A_1^0 = Activity of ^{210}Pb at time of separation, in Bq

A_3 = Activity of ^{210}Po at time of mid-count, in Bq

A_1 = Activity of ^{210}Pb or ^{210}Bi at time of mid-count, in Bq

λ_1 = ^{210}Pb decay constant, in sec^{-1}

λ_2 = ^{210}Bi decay constant, in sec^{-1}

λ_3 = ^{210}Po decay constant, in sec^{-1}

t = Ingrowth time, in sec

3. Results and discussion

3.1. Analytical Set 1

Analyses performed in Set 1 yielded inconsistent results. Yields for ^{203}Pb tracer varied greatly, from a high of 59.7%–0% in the final precipitate. Stable Pb carrier was also inconsistent and very low as well. Interestingly, ^{203}Pb was observed on the Pb Resin columns using a handheld Geiger Muller counter after final elution and not in the initial column eluate. This indicates that Pb loaded on the columns was not efficiently eluted.

Deionized water was used as the final column eluent and appears to be the culprit of the inefficient removal of Pb from Pb Resin. In preliminary tests of ASTM D7535, deionized water from another source (an entirely different water purification system) was utilized and

the method appeared to work well. pH measurements performed showed a substantial difference between the eluent used in Set 1 (pH 5) and the eluent used in preliminary analyses (pH 7). These experiments led us to consider the use of a more carefully pH controlled buffer system for elution of Pb from the Pb-resin chromatography column.

3.2. Analytical Set 2

To address the issues encountered in Set 1, 0.25 M sodium citrate was used *en lieu* of deionized water as the final eluent for its buffering capacity. Set 2 tracer yields were significantly better ($79 \pm 10\%$) across all matrices, with ($87 \pm 4\%$) or without ($72 \pm 9\%$) stable Pb carrier added to the samples. Samples containing stable Pb carrier showed slightly higher ^{203}Pb tracer yields (Produced Fluid: $87 \pm 3\%$ vs. $75 \pm 6\%$; River Water: $83 \pm 3\%$ vs. $70 \pm 7\%$; Tap Water: $90\% \pm 1\%$ vs. $80 \pm 4\%$) (Table 1).

3.2.1. Simple matrices (river and tap water)—Tracer (^{203}Pb) and stable Pb yields were mostly comparable in simple, low-endogenous-Pb matrices (river water and tap water, for which the original ASTM D7535 method was designed) in subset C, where both stable Pb and ^{203}Pb were added. In these samples (river and tap water) ^{203}Pb tracer yields averaged $87 \pm 5\%$ and stable Pb yields averaged $94 \pm 6\%$, for these two matrices. Recovered activities of ^{210}Pb were also comparable in subset C, with ^{203}Pb -corrected activities averaging 0.81 ± 0.03 Bq ($90 \pm 4\%$ Recovery) and stable Pb-corrected recoveries averaging 0.76 ± 0.02 Bq ($84 \pm 3\%$ Recovery) (Table 1).

Across all subsets for simple, low-Pb matrices, ^{210}Pb recovered activities were comparable between ^{203}Pb -corrected, averaging 0.82 ± 0.04 Bq ($91 \pm 5\%$ Recovery), and stable Pb-corrected, averaging 0.75 ± 0.03 Bq ($83 \pm 3\%$ Recovery), analysis groups, with ^{203}Pb -corrected recovered activities being slightly closer to the fortified activity (Table 1). As a result of these data, it appears that Pb lead carrier is not required for chromatographic separations and utilizing ^{203}Pb as a radiochemical tracer works just as well, if not slightly better than stable Pb carrier-based yield corrections.

3.2.2. Complex matrix—The analysis of Marcellus Shale hydraulic fracturing produced fluid yielded some interesting complications. Yields for stable Pb carrier and ^{203}Pb tracer were significantly different (*t*-test, $p < 0.05$) for subset C, averaging $104 \pm 6\%$ and $87 \pm 3\%$, respectively (Table 1). The difference between these yields for produced fluid and those of tap and river water was compared using an analysis of variance (ANOVA), showing a significant difference ($p > 0.05$) between the three sets, with produced fluid having the greatest difference between the two recovery methods. There was no statistically significant difference observed for the tap and river water matrices. There is a non-trivial amount of stable Pb (1.0 mg/L), as well as 36,000 mg/L Sr, 9000 mg/L Ba, 147,000 mg/L Cl, and an extremely high level of dissolved solids (278,000 mg/L) present in this produced fluid (Nelson et al., 2014). While lead is much more strongly retained on Pb-Resin across all concentrations of nitric acid than either Sr or Ba (Horwitz et al., 1994), their extraordinarily high concentrations mean that a significant amount of both of these ions are likely to be retained and co-elute with Pb. All three of these divalent cations precipitate with the addition of sulfuric acid, as used in the ASTM D7535.

As a result of this interference, final calculated recovered activities were very different across all subsets, with stable Pb-corrected activities of ^{210}Pb (3.73 ± 0.36 Bq) lower than ^{203}Pb -corrected activities of ^{210}Pb (2.85 ± 0.04 Bq). Recoveries were much greater than 100% due to the large amounts of ^{210}Pb present in the produced fluid analyzed; the concentration present in the matrix was not determined in analytical Set 2 and the results of the spiked samples were not corrected for the matrix contribution.

As ^{203}Pb is not susceptible to interference from high Pb-Sr-Ba containing matrices, it appears to be the better choice for yield correction when analyzing this type of sample. Stable Pb yield correction may be used on complex samples, but extra analyses must be performed to determine and correct for the presence of endogenous Pb, Sr, and/or Ba in each sample, adding substantial analytical burden and uncertainty the final measurement result.

3.3. Analytical Set 3

With analytical Set 3, LSC was chosen to reduce sample handling and completely eliminate stable Pb from the process. As a result of the elimination of stable Pb, much smaller columns were prepared as we were no longer concerned that stable Pb would overload the binding capacity of the resin. Larger 2 mL columns were only necessary to accommodate stable Pb carrier, due to the relatively low resin capacity of 20.5 mg Pb per mL of Pb resin bed (Horwitz et al., 1994). We found that sodium citrate, at the concentrations used for analytical Set 2, (i.e., 5 mL, 0.25 M) clouded Ultima Gold AB scintillation cocktail. Therefore, the final column eluent was changed to 0.2 M ammonium acetate, as ammonium acetate provides similar buffering capability to sodium citrate, and is listed as an reagent compatible with Ultima Gold AB scintillation cocktail (Thompson and Burns, 2014).

Tracer yields for both matrices (produced fluid and deionized water) were excellent, averaging $83 \pm 8\%$ overall, with slightly better yields for deionized water ($89 \pm 5\%$) versus produced fluid ($76 \pm 6\%$) (Table S1). This may be due to the extremely high levels of Sr, Ba, and Ca competing with Pb sorption onto the Pb resin. A very small volume of Pb resin, 0.25 mL, was still able to handle a solution of extremely high solute concentration and return excellent yields.

^{210}Pb recoveries were excellent overall, using either the ^{210}Pb window or the ^{210}Po window, averaging $95 \pm 11\%$ and $91 \pm 11\%$, respectively. There was no significant difference in average recoveries between produced fluid ($93 \pm 16\%$ and $93 \pm 13\%$) and deionized water ($98 \pm 6\%$ and $90 \pm 9\%$) using either of the two windows (Table S1). It appears that utilizing the ^{210}Pb window may yield slightly better results and a lower minimum detectable activity (MDA) at 3 weeks the ^{210}Po window. With a longer ingrowth period the ^{210}Po window may yield a lower MDA due to the substantially lower background observed, while the MDA for the ^{210}Pb window will remain essentially unchanged (Table S2). Either counting window may be used, with the ^{210}Bi window showing slightly less bias.

3.4. Liquid scintillation versus gas-flow proportional counting

The use of LSC simplifies nearly all components of this analysis. Preparation of calibration curves for GPCs, as well as the need to calibrate multiple detectors (if using multi-detector systems) adds to the complexity of the analysis, while calibration for LSC requires much

less time and effort. The increased handling required for GPC increases the potential for contamination of samples from external sources and contamination of instrumentation by samples, as well as potential for loss of sample during handling.

Using the instrumentation and approach presented here, gas-flow proportional counting holds one advantage over liquid scintillation, in that detection limits for GPC tended to be lower than LSC, due primarily to the lower background count rates achievable using the systems available. Under similar counting durations at 3 weeks after separation, LSC shows a 3–4-fold greater detection limit than GPC; at 3 months, the difference in detection limits decrease to a 2–3-fold difference (Table S2). Depending on application, this difference in detection limits may drive counting methodology selection, but this separation and yield correction methodology can also be applied to GPC if desired. And the elimination of stable lead carrier should not require a calibration curve to be prepared; a set of point sources could be utilized instead, simplifying the analysis. Further studies are needed to determine if lower-background LSC instrumentation could be used to improve detection limits achievable using the ^{203}Pb tracer approach.

4. Conclusions

While traditional methods for ^{210}Pb analysis (*e.g.*, ASTM D7535) provide a relatively accessible approach for the analysis of ^{210}Pb in simple matrices, complex matrices and matrices that contain high levels of Pb (*e.g.*, hydraulic fracturing produced fluids) can confound these approaches. The application of ^{203}Pb as a radiochemical tracer for ^{210}Pb analysis solves the interferences present in complex matrices. The radiochemical properties of ^{203}Pb allow for its use at relatively high activities to generate excellent counting rates (and low counting uncertainties) without concern for generation of a high activity waste stream ($t_{1/2} = 51.92$ h); the authors can make ^{203}Pb available to interested parties with appropriate radiation safety licensing. The short half-life of ^{203}Pb can also be a potential drawback of this approach, as this material must be regularly reacquired; this may make this method most suitable to analyzing large numbers of complex samples at one time.

Additionally, the elimination of stable Pb carrier from the method allows smaller column volumes and the use of LSC. This critical development allows for higher counting efficiencies, potentially lower counting errors, and higher throughput with less tedious technical work. Furthermore, the reduction in column volume allows direct elution of ^{210}Pb -containing eluate into the final counting container, reducing elution duration, and risks of contamination during handling. The resulting improved method is more robust than traditional methods (*e.g.*, ASTM D7535), extending the range of applicability to even the most complex matrices. We suggest this new method, as outlined in Fig. 3, will be particularly helpful for ^{210}Pb samples containing high quantities of lead, barium, and strontium.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Ingrowth and decay behavior of lead-203, lead-210, bismuth-210, and polonium-210. (A) 138 Days, (B) 30 Days, (C) ^{203}Pb at 10 times activity, (D) ^{203}Pb at 1000, 100, 10, and 1 times activity.

Fig. 2.

Analytical Set 3, lead-203 tracer yields and lead-210 recoveries. Lead-203 tracer yields are shown for both fortified and blank matrices, lead-210 recoveries are shown when using ^{210}Bi and ^{210}Po to calculate lead-210 activity. Each set was analyzed in quadruplicate, error bar represent the standard deviation of the set.

Fig. 3.
Method flowchart.

Table 1

Analytical set 2 ^{203}Pb tracer yields and ^{210}Pb recoveries. Analyses were performed in triplicate with standard deviations reported for each analysis condition; “Y” indicates that either ^{203}Pb and/or stable Pb carrier were/was added prior to any chemical separation, “N” indicates the absences of either ^{203}Pb and/or stable Pb carrier.

	Pb-203	Stable lead	Yield		Activity (Bq)	
			Pb-203	Stable lead	Pb-203	Stable lead
Produced Fluid	Y	N	75 ± 6%	–	4.02 ± 0.24	–
	N	Y	–	102 ± 3%	–	2.84 ± 0.03
	Y	Y	87 ± 3%	104 ± 6%	3.44 ± 0.05	2.86 ± 0.05
River Water	Y	N	70 ± 7%	–	0.84 ± 0.03	–
	N	Y	–	92 ± 8%	–	0.74 ± 0.03
	Y	Y	83 ± 3%	88 ± 2%	0.80 ± 0.04	0.75 ± 0.04
Tap Water	Y	N	80 ± 4%	–	0.81 ± 0.07	–
	N	Y	–	95 ± 0%	–	0.75 ± 0.04
	Y	Y	90 ± 1%	99 ± 0%	0.83 ± 0.02	0.77 ± 0.00