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AN EFFICIENT QUANTITATIVE TECHNIQUE FOR THE SIMULTANEOUS ANALYSES OF RADON DAUGHTERS ^{210}Pb, ^{210}Bi AND ^{210}Po

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Summary—An improved and time efficient technique has been developed for quantitative determination of the long-lived ^{222}Rn daughters (^{210}Pb, ^{210}Po and ^{210}Bi) in atmospheric and oceanic samples. The sample is first spiked with yield tracers for polonium (208 or 209), bismuth (207), and lead (stable lead carrier). These nuclides may then be scavenged through iron hydroxide precipitation and redissolved in a dilute (pH ~ 2) nitric acid plating medium with citrate and hydroxylamine hydrochloride at 90° centrigrade with constant stirring. First a silver planchet is suspended in the solution which plates polonium to high efficiency. Second, a nickel planchet is suspended in the same solution which is maintained hermetic (*e.g.* bubbling with helium) and bismuth is plated next with high efficiency. Third, lead is purified from the same solution using anion exchange techniques and isolated for beta counting as the sulfate. Polonium is analyzed by isotope dilution alpha spectrometry. Bismuth and lead are analyzed by anti-coincident beta counting in a low level shield. In the case of bismuth, the 207 tracer is added in quantities at least comparable to the background of the beta system such that counting before and after the decay of ^{210}Bi gives the bismuth yield.

The unique characteristics of this technique are its speed and efficiency; all three radon daughters can be isolated for counting within 4 hr of pre-treating the sample. The remaining solution can be treated subsequently for other analyses as appropriate.

Daughter products of ^{222}Rn (Fig. 1) are useful tracers in the studies of several geochemical and health related processes.[1,2] One widely used atmospheric application of these isotopes is in the study of the atmospheric residence time of aerosols in the troposphere,[3] via ^{210}Po/^{210}Pb and ^{210}Bi/^{210}Pb activity ratios.[4–6] In groundwater geochemistry, measurements of these nuclides have helped to evaluate the reactive behavior of geochemical analogues (*e.g.* the retardation rate constants) and to assist in making site specific models of transport of such species.[7–12] In health related issues, measurements of these nuclides are important due to their radiotoxicities.[13,14]

Several techniques for the simultaneous determinations of Pb, Bi and Po are available in the literature. For example, Marckwald[15] found that polonium deposited very readily onto silver from dilute hydrochloric or nitric acid. Curie and Debierne[16] established the separation of Po from Pb by spontaneous deposition on copper. Subsequently, other workers[2,13,17–19] refined the techniques for the separation and deposition of Po and Bi using Ni planchets. Narita *et al.*[20] devised an electrodeposition cell for the separation of Bi for which they used stable Bi carrier to quantify the Bi yields.

One important problem in ^{210}Bi determinations is the appropriate choice of a yield tracer. Use of stable Bi as a carrier chemically complicates the recovery and limits the number of analyses per unit time. Although, the procedure of Narita *et al.*[20] is relatively time efficient, it is labor intensive. In this paper we describe a simple technique that utilizes a radioactive isotope of Bi (^{207}Bi, half-life = 38 years) as yield tracer and the ability to quantitatively separate Po and Bi by spontaneous sequential deposition on silver and nickel planchets, respectively. Specifically, the sample, taken in a suitable medium as discussed later, is first plated for Po on a silver disc.[21] A nickel planchet is then introduced in the solution and Bi is then

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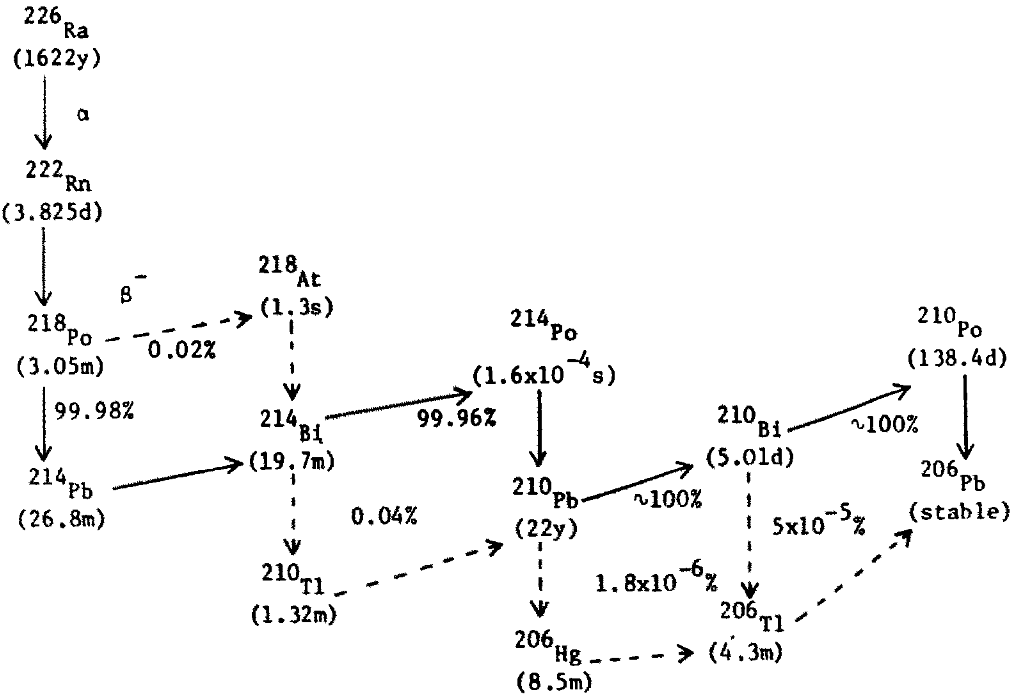

Fig. 1. ^{222}Rn daughter series taken from Moore et al.[30]

isolated subsequently.[22] Finally, lead is processed using standard techniques which isolate and count the sulfate.[23]

Yield tracers

Quantitative analysis of nuclides requires the samples to be spiked with yield tracers or carriers which are not naturally present in the samples in the amounts added. The nuclide recoveries in the prepared solutions are then followed to estimate the yield.[24] The Po isotopes, ^{208,209}Po, serve as good spikes for Po, and stable Pb as $Pb(NO_3)_2$ is good as a Pb-carrier. However, a suitable choice of Bi spike poses some problems. The nuclide of interest, ^{210}Bi, emits a 1.4 MeV beta which is easily detected by a gas-flow type Geiger counter.[25] There are several isotopes of Bi that are artificially produced and are gamma or alpha active which may be employed as tracers. However, these isotopes or their short-lived daughter products interfere with beta countings, measured as total beta activity, in the Geiger region. Also, the particle energies of beta emitters are generally continuous over a wide range which precludes the use of a proportional counter coupled to multichannel analyses.

^{207}Bi (half-life = 38 years) is mainly a gamma emitter (570 keV, 97%; 1064 keV, 76% and 1770 keV, 8%). It emits a conversion electron at 960 keV with 25% intensity. Since the conversion electrons are nearly monoenergetic, they show a relatively sharp peak in multichannel analysis (Fig. 2). We have, therefore, used ^{207}Bi to trace the Bi yields in this procedure for measuring ^{210}Bi.

Extraction procedures

Pilot experiments were carried out with known amounts of mixed standards having ^{210}Pb, ^{210}Bi and ^{210}Po in equilibrium in order to develop procedures for extracting the radionuclides. Known quantities of these standards are mixed with Pb-carrier (equivalent to about 50 mg of $PbSO_4$), Fe-carrier (30 mg $FeCl_3$) and ^{208}Po and ^{207}Bi spikes.

The quantity of ^{208}Po spike is kept approximately equal to the expected activity of ^{210}Po in the sample. However, the activity of added ^{207}Bi is always kept at 4.2 dpm (equivalent to 22 net counts/hr on our beta counter with a background of 15 counts/hr). Samples are dried and taken in 0.1*M* HCl medium with 5 ml of 20% hydroxylamine hydrochloride and 2 ml of 25% sodium citrate solutions, added in order to prevent iron from plating. The solution is adjusted to pH 2 with a few drops of ammonium hydroxide solution. Polonium is plated first on a polished silver planchet at 85–90°C over 3 hr with constant stirring. A nickel planchet is next

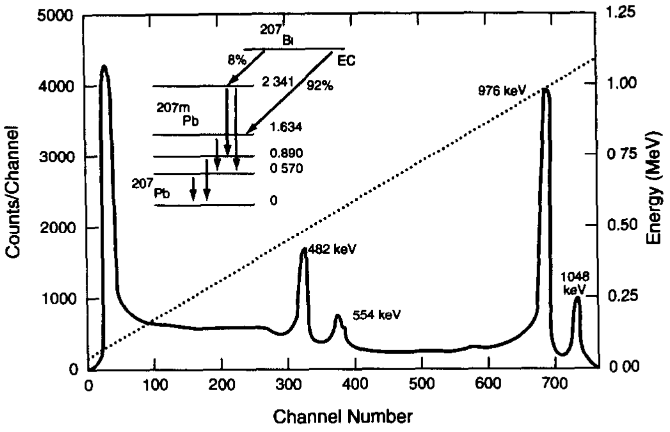

Fig. 2. ^{207}Bi conversion electron spectrum. The intensity of the conversion electron at 976 keV is 25%. The dotted line shows energy calibration of the fully depleted silicon surface barrier detection with 1500 μm depletion thickness (1.4 keV/channel) used in this study.

placed into the solution and a further 4 hr is allowed for hermetic Bi plating at around 95°C. After the plating is complete, the nickel planchet is removed and washed hermetically with hot water just previously boiled. In air, including aerated solutions, adsorbed Bi quickly gets removed from nickel[2,13] and therefore care must be exercised in removing and washing the nickel planchet.

The remaining solution is taken to dryness, repeatedly oxidized with HNO_3 and taken up in dilute HNO_3. Ammonium acetate is then added to give the solution pH ~ 4, and $PbCrO_4$ is precipitated by adding 2 ml of 2% $NaCrO_4$ solution. After washing with distilled water, the chromate precipitate is dissolved in 1.5*M* HCl and passed through previously conditioned anion exchange resin column to purify the lead.[7] Lead is eluted with hot distilled water, converted to $PbSO_4$ with a drop of H_2SO_4, filtered, ignited, weighed and deposited on a Plexiglass holder for beta counting.

Natural samples

In the case of groundwater, seawater, rainwater or sediment samples, the procedure may be suitably modified. For example, after adding and equilibrating the spikes/carriers to large quantities of water samples, the Pb, Bi and Po isotopes may be preconcentrated by coprecipitating on $Fe(OH)_3$ following procedures well known for other U–Th series nuclides[23,26] and the precipitate dissolved in dilute HCl before radon daughter assay. Sediment samples may be digested with HF + $HClO_4$ and taken in dilute HCl after a complete fuming of $HClO_4$. The remaining procedure of extracting and plating Po, Bi and Pb remains the same as described above. The schematic of the analytical procedure is shown in Fig. 3.

In an effort to understand the source of low Bi yields in some of our experiments, we observed that high molarity of HCl solutions produce low yields. Nickel planchets also dissolve to a certain extent under high chloride contents of the plating solution. This was especially noticed while working with seawater samples. Conversion of chlorides into nitrates and taking the final solution in 0.1*M* HNO_3 gave better Bi yields without any planchet dissolution but reduced Po yields by about 25%. More work on the effect of chloride contents on Bi yields and related nickel dissolution is in progress and will be reported later.

Counting methods

Polonium sources are counted via their alpha activities using silicon barrier detectors coupled to a multichannel analyzer.[27] Lead sources are beta counted via ingrowing ^{210}Bi[7] after which the growth of ^{210}Bi is followed over a period of about a month to ensure the purity of the source.[28] Low energy beta particles from ^{210}Pb (about 15 keV) are eliminated by a mylar absorber covering the source (0.9 mg/cm^2). All analyzed samples showed excellent purity by following the expected growth at a half-life of ^{210}Bi with a correlation coefficient in excess of 0.97% similar to that shown in Fig. 4.

Bismuth sources are counted with a 6 mg/cm^2 gold mylar on the beta counter in a similar manner as ^{210}Pb sources. Since absorption of high energy particles by a media is density and thickness dependent, the general convention is

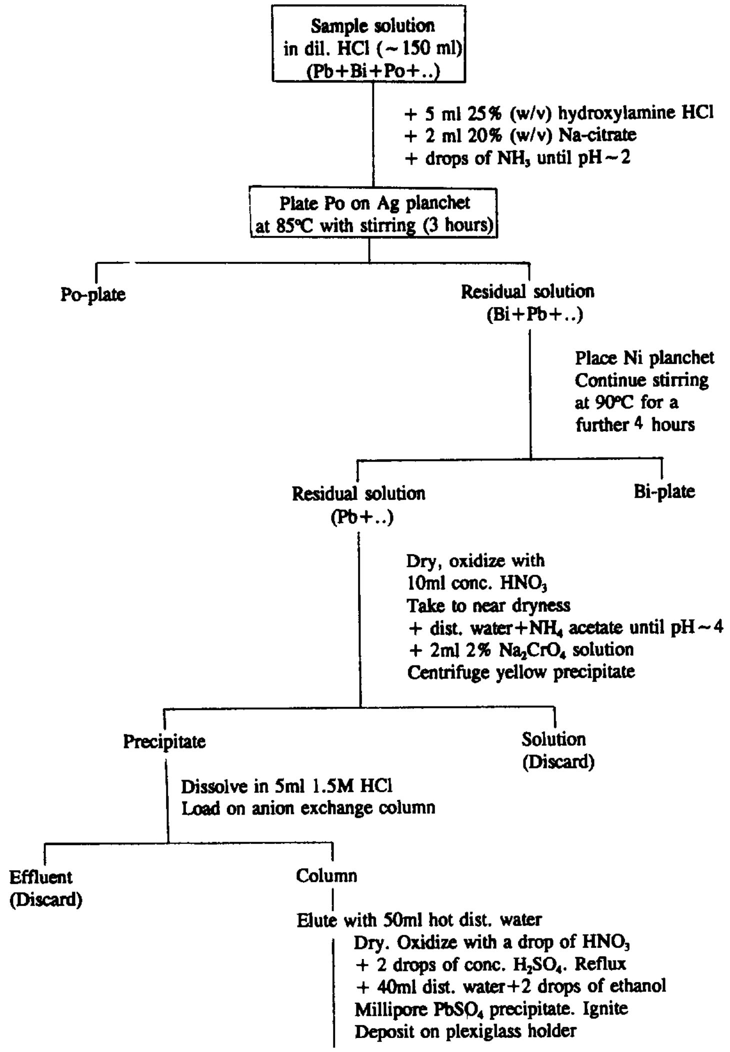

Fig. 3. Flow chart of the chemical procedure used in this study.

to express radioactive absorbants as mg/cm^2 units rather than cm. The mylar is used to eliminate alpha particles from Po, if any, on the source. In this case, since there is no ingrowth of ^{210}Bi from ^{210}Pb, the activity on the planchet would start to decay with the half-life of ^{210}Bi. The decay of ^{210}Bi is followed over a period of about a month. Decay curve analysis is used, as in case of ^{210}Pb, to check the purity of the source. At times exceeding a month (six half-lives of ^{210}Bi), when more than 98% of the ^{210}Bi has decayed away from the source and only ^{207}Bi is left over, the planchet is beta counted again. It is then assumed that the remaining activity is due to ^{207}Bi alone and may therefore be used to evaluate the chemical yield (Fig. 4).

Assumption that the remaining activity on the nickel planchet is due to ^{207}Bi necessitates assuring the purity of the Bi source. Any longer lived beta emitting nuclide present on the planchet would tend to increase the estimated Bi yield. Although some information on the purity of any given source may be obtained from the decay curve of ^{210}Bi, two other independent measurement techniques have been used to verify this assumption in a variety of atmospheric and oceanic samples from the CHESS Cruises in the slope sea of the northwestern mid-Atlantic and ATLANTIS II Cruise on Juan de Fuca Ridge in the coastal Pacific off Oregon (see Field Samples section). In the first technique, a silicon surface barrier detector was used to obtain the spectrum of the conversion electron from ^{207}Bi, and in the second technique ^{207}Bi was measured directly via its gamma emission.

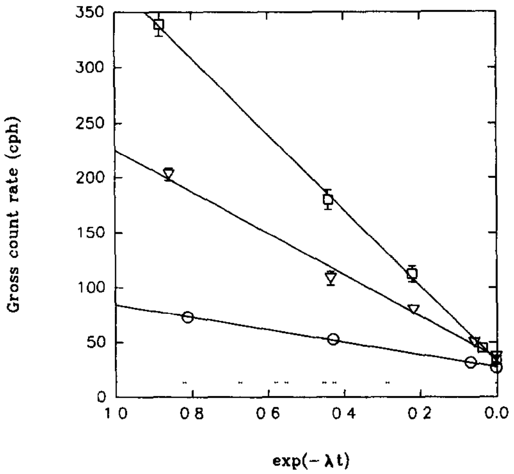

Fig. 4. Decay curves obtained from the beta countings of Bi plates. ○—represents data from Experiment-I, ▽—Experiment-II and □—Experiment-III. Uncertainties in activities larger than the size of the symbols, are shown by the error bars. Excellent fit to the data shows high purity of the plates. Excess intercept over the background, represented by the dotted line, is used to estimate the chemical yield.

USE OF A SURFACE BARRIER DETECTOR

To verify the purity of residual gross beta counting due only to ^{207}Bi, we utilized a surface barrier detector in the Bi-yield determinations. The main difficulty of using a surface barrier detector in beta spectroscopy is the large range of beta particles which necessitates detectors with thicker depletion depths (EG & G, 1984). Also, because the excitation energy in a beta decay is shared by the beta and gamma particles, there is generally a continuum of beta energies from a beta source. Energy spectra from such sources do not show a discrete energy peak, but instead are characterized with β_{av} and β_{max}. Conversion electrons, on the other hand, are produced due to internal conversion processes when a nucleus imparts its energy of excitation directly to one of its nearby orbiting electrons and the electron then leaves the atom with a discrete energy. Energy spectra from such sources do show strongly discrete energy peaks and permit a direct measurement through multichannel gamma spectroscopy (Fig. 2).

As discussed earlier, ^{207}Bi emits a conversion electron at 960 keV. The range *vs* energy curve for beta particles in silicon[29] suggests a depletion thickness of nearly 1500 μm for its total absorption. A totally depleted silicon surface barrier detector from EG & G (Model No. BB-021-300-1500), coupled to MCA was used to obtain the count rate of ^{207}Bi in some of the sources for cross check purposes. A typical count rate due to ^{207}Bi ranged between 15 and 20 cph over a 10 cph background. Chemical yield estimated through this procedure was within 10% of the reported values (Table 1), determined through the conventional total beta countings using gas flow type Geiger counters. Although yield determinations using a surface barrier detector are advisable for better accuracy, the high cost of the detector ($4000) discourages its use when the total beta counting yields results within 10%.

Table 1. Recovered activities of ^{210}Pb, ^{210}Bi and ^{210}Po by the simultaneous determination technique. Known amounts of ^{210}Pb spike, in equilibrium with ^{210}Bi and ^{210}Po were used as pilot experiments in developing the extraction technique

Expt. No.	Added activity (*dpm*)	Recovered activities (*dpm*)		
		^{210}Pb	^{210}Bi	^{210}Po
1	4.0	4.3 ± 0.5	4.3 ± 0.1	3.5 ± 0.1
2	8.0	9.2 ± 1.2	8.8 ± 0.5	9.7 ± 0.3
3	16.0	16.1 ± 0.1	17.9 ± 0.3	15.1 ± 0.3

USE OF A Ge DETECTOR

The ^{207}Bi also emits three gamma rays with emission at 570 keV, 1064 keV and 1770 keV, of which the particle at 570 keV is the most intense (97%). This may be detected using a low background Ge detector.

An intrinsic germanium coaxial detector from Princeton Gamma Tech, Inc. (Model No. NIGC 2020) was used for measurements of ^{207}Bi. The overall counting efficiency at 570 keV for a weightless ^{207}Bi source on nickel was 2.9%, and at 1064 keV, 1.5%. However, the signal to background ratio still remained below 2 because the added ^{207}Bi spike was kept low at 4.2 dpm. This could be improved by adding higher amounts of ^{207}Bi to the samples. Thus, two and a half fold greater amounts of ^{207}Bi were added to the samples from the ATLANTIS II cruise. In these samples, the yield estimate based on gamma spectroscopy was within 5% of results from beta spectroscopy and total beta measured on Geiger counters (Table 3). Generally, the goal is to obtain a better initial ^{210}Bi/^{207}Bi count

Table 2. Chemical yields of ^{210}Pb, ^{210}Bi and ^{210}Po determinations, and correlation coefficients from the least squares regression analyses on ^{210}Bi activities (ingrowth in case of pure ^{210}Pb sources and decay of pure ^{210}Bi for the pilot experiments)

Expt. No.	Chemical yield (%)			Correlation co-efficient	
	^{210}Pb	^{210}Bi	^{210}Po	^{210}Pb	^{210}Bi
1	75.2	61.0	21.4	0.99	0.99
2	73.6	99.9	67.8	0.98	0.99
3	73.1	89.9	95.4	0.99	0.99

Table 3. Comparison between chemical yields for Bi determined through residual beta activities and gamma spectrometry of ^{207}Bi

Sample ID	Chemical yield (%) Beta	Chemical yield (%) Gamma
Rn Filter #1	100.9 ± 21.4	103.4 ± 3.6
Rn Filter #3	84.5 ± 5.4	82.0 ± 2.5
Rn Filter #13	99.3 ± 10.8	96.8 ± 3.4
ALV2464-W1(1)	88.3 ± 5.6	86.5 ± 3.2

rate ratio and an acceptable ^{207}Bi count rate to the background ratio at the time when ^{210}Bi is all decayed away. As such, one must have some knowledge of the *in-situ* ^{210}Bi activity in the sample and then add approximately an equal amount of ^{207}Bi.

RESULTS AND DISCUSSION

Calibration experiments

Results of the simultaneous determinations of Pb, Bi and Po in the calibration experiments using known activities of ^{210}Pb in standard solutions to develop the extraction techniques are presented in Tables 1 and 2. The errors quoted in Table 1 are uncertainties due to 1σ counting statistics. The ^{210}Pb in the Axel Standard used in these experiments was in equilibrium with its daughters. The expected activities of ^{210}Bi and ^{210}Po in each experiment, therefore, were equal to the added ^{210}Pb activity. All the recovered activities are within 15% of the added activities. An exception is in Experiment-I (Table 1) which is about 19% lower than the expected value and may be due to an unusually low chemical yield (Table 2).

Chemical yields presented in Table 2 on ^{210}Pb and ^{210}Po are evaluated based on the recovery of stable Pb carrier and ^{208}Po spike, respectively. The Bi yields are evaluated based on the intercept of the ^{210}Bi decay *vs* count rate (cpm) plots (Fig. 4) after correcting for the counter background. Yields in excess of about 70% are common in our laboratory.

Values of the correlation coefficients close to unity in the growth or decay curve analyses of ^{210}Pb or ^{210}Bi (Table 2), suggest high purity in the separation of these nuclides for these experiments (Fig. 4). Such separation is especially important for Bi because any residual activity at large times after plating that is not due to ^{207}Bi may affect the estimate of the chemical yield as determined by total beta counts. As discussed earlier, the level of beta activity due to ^{207}Bi was kept to just over 100% of the counter background. It is possible to keep this several times over the background count rate provided the signal due to ^{210}Bi in the sample is expected to be larger. In any case, for unambiguous results, it is suggested to keep the initial count ratio of ^{210}Bi/^{207}Bi over 5. Larger added activities of ^{207}Bi spike would also tend to reduce the sensitivity for error due to contamination of Bi plates.

Field samples

The technique of ^{210}Pb, ^{210}Bi and ^{210}Po analyses was used for aerosol and submarine hydrothermal vent samples collected from the Juan de Fuca Ridge. Samples were stored for over two months before processing so that equilibrium between ^{210}Pb and ^{210}Bi was assured. Also, an order of magnitude higher ^{207}Bi concentrations were used as spikes as the anticipated activities would be higher than normal aqueous samples. An excellent correlation between measured ^{210}Pb and ^{210}Bi in equilibrated samples of aerosol and hydrothermal vents from Juan de Fuca Ridge (Fig. 5) suggests the wide applicability of the technique for the simultaneous and quick determinations of the radon daughter nuclides in natural marine and atmospheric samples.

CONCLUSIONS

A simple improved and time efficient technique has been developed for the simultaneous determination of the long-lived ^{222}Rn daughters (^{210}Pb, ^{210}Bi and ^{210}Po). The method relies on the spontaneous sequential plating of the Po and Bi daughters and use of yield tracers ^{207}Bi, ^{208}Po or ^{209}Po and stable Pb carrier.

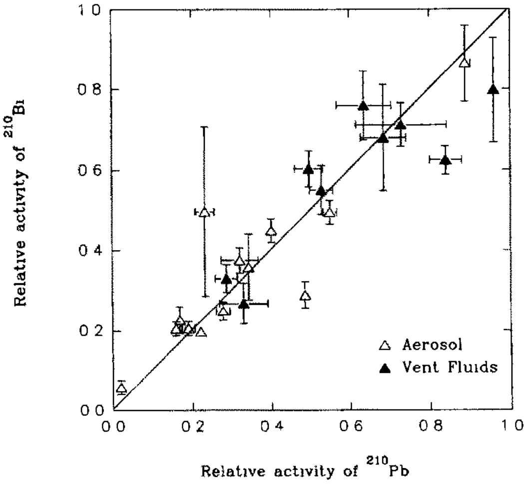

Fig. 5. Regression of ^{210}Pb activity, measured via conventional technique, and ^{210}Bi activity, measured via the reported technique. The correlation co-efficient of 0.99 supports the application of the technique for measuring ^{210}Bi in natural aerosol and hydrothermal vent fluids.

It must be noted that when using a Geiger counter in ^{207}Bi yield determinations, care must be taken to ensure the purity of the Bi plate. Any long-lived beta or low energy gamma emitters present on the plate would tend to overestimate the Bi yields. The possibility of such an interference could be high in case of complex samples like seawater. At present we do not know of any natural U and Th series radionuclides, with the exception of Po, which co-plates with Bi on nickel planchets under the plating media described above. Checking the purity of ^{207}Bi signal through multichannel beta or gamma spectrometry would certainly be helpful.

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