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The Mass Spectrometric Determination of Fallout ^{239}Pu and ^{240}Pu in Marine Samples

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ABSTRACT

A thermal ionization mass spectrometric technique is presented for the detection of ^{239}Pu and ^{240}Pu in sea water, pore water, ocean sediments, sediment trap samples and coral samples. Both sample preparation and purification procedures, as well as the procedure used to detect Pu by mass spectrometry (m.s.), are presented. The m.s. technique proves to be over an order-of-magnitude more sensitive than traditional alpha-counting techniques for the detection of Pu in environmental samples. Also, the ratio of ^{240}Pu/^{239}Pu is obtained with this technique.

INTRODUCTION

Plutonium (Pu) was introduced to the oceans predominantly in the 1950s and early 1960s as fallout from the atmospheric nuclear weapons testing programs (Harley, 1980; Perkins & Thomas, 1980). Since this time, plutonium has been used by oceanographers as a geochemical tracer to study removal processes in the water column and in understanding mixing processes in marine sediments (see Sholkovitz, 1983 for review). In general, geochemical researchers have measured fallout Pu by standard alpha-counting techniques. This results in the determination of ^{239,240}Pu, which

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represents the combined activity of the two most common fallout Pu isotopes, ^{239}Pu and ^{240}Pu (these isotopes being inseparable when Pu is determined by alpha-counting). An alternative Pu detection technique is thermal ionization mass spectrometry (m.s.), which has been shown to be highly sensitive and capable of separating the ^{239}Pu and ^{240}Pu isotopes (Strebin & Robertson, 1977; Halverson, 1981; Perrin *et al.*, 1985). We have applied a mass spectrometric technique for the determination of fallout Pu concentrations and isotopic ratios in sea water, ocean sediments, pore waters, sediment trap material and coral samples. The optimal procedures used for the preparation and analyses of Pu by thermal ionization m.s. in these samples will be presented.

THERMAL IONIZATION MASS SPECTROMETRY

The mass spectrometer (m.s.) used in this study is operated by E. I. DuPont de Nemours & Co. at the Savannah River Laboratory (S.R.L.) in South Carolina. The instrument was designed and built similar to other mass spectrometers within the national labs to fit the necessary requirements for trace level Pu isotopic analyses (Lagergren & Stoffels, 1970). A complete description of the m.s. is given by Halverson (1981) and is briefly summarized below.

The instrument is designed in a three-stage arrangement consisting of two identical magnetic analyzers (90°, 30·5 cm radius) in a 'C'-configuration, followed by an electrostatic analyzer (90°, 30·5 cm radius) and an ion-multiplier type detector. The source is a 'canoe'-shaped single Re-ribbon. The instrument is interfaced with a PDP 11/34 computer for automated mass stepping (accomplished by sweeping the accelerating voltage) and data acquisition. The instrument is housed in a 'Class 100' clean-room facility where all of the filament fabrication and sample loading occur. Samples can be loaded into the vacuum system, five at a time. One of the filament positions is occupied by a uranium standard (NBS U standard U005), which can be repeatedly used at the start of a given run to align the beam by focusing of the ^{235}U and ^{238}U mass peaks. Up to four samples can then be analyzed within a period of two to three hours.

Source and loading

The source filament arrangement is a critical component of any m.s. set up since the ability to efficiently form Pu ions at the source determines, to a large extent, the overall detection efficiency (typically 0·1–1% for these samples). The filament ribbon is made from a strip (0·12 cm wide) of triple zone-refined Re which is folded into a v-shape. The ends of the ribbon are then pinched and the ribbon is spot welded on to the tungsten posts of the

filament base forming a 'canoe'-shaped source filament. The assembled filaments are baked at 1500°C for 30 min under vacuum to ensure a clean source. The filaments are then ready to be carburized.

The effects of carburization on the thermal ionization of Pu off Re filaments have been well studied (Pallmer *et al.*, 1980*a*, *b*; Kelley & Robertson, 1985). In general, carburization refers to the deposition of a carbon source onto a m.s. filament. Carburization increases the work function of the Re ribbon, resulting in an improvement in the efficiency of Pu ion production off the m.s. filament (Pallmer *et al.*, 1980*a*; Kelley & Robertson, 1985). As a reducing agent, the carbon also serves to promote the production of Pu ions over Pu oxides, the latter being undesirable for m.s. analysis (Studier *et al.*, 1962; Kelley & Robertson, 1985). Furthermore, the presence of carbon has been shown to counteract Pu diffusion on the filament surface so that a point source for good ion optics is maintained (Smith *et al.*, 1980).

At S.R.L., the carburization procedure is as follows: a current is run through a series of up to eight m.s. filaments that are held in a vacuum chamber ($p < 5 \times 10^{-6}$ torr). The current is raised slowly until the temperature of the filaments reaches ~1050°C, as determined by an optical pyrometer. A valve on a trap containing xylene in a dry ice and alcohol bath is opened until the chamber pressure reaches 5×10^{-5} torr. This allows for leakage of xylene vapor into the chamber. The xylene vapor serves as the carbon source that is deposited on to the hot Re filaments. The extent of carburization is controlled by stopping the xylene flow after 30 min has elapsed. Once carburized, the filaments are returned to room temperature and pressure after closing the valve to the xylene trap and reducing the current to zero. This carburization procedure has been successfully performed on filaments that are either loaded or unloaded, i.e. either with or without a sample being in place on the filament prior to carburization. We have not found any major difference in the observed ionization efficiency between these two options.

The actual sample is loaded on to the filament as two anion-exchange beads that are placed in the center of the filament trough. The resin bead technique was first described by Freeman *et al.* (1970) and first reported for use in the determination of U and Pu by m.s. by Walker *et al.* (1974). Plutonium samples loaded as resin beads have up to an order-of-magnitude increased ionization efficiency when compared to Pu samples loaded as solutions (Smith *et al.*, 1980). We have also found that the bead technique provided higher ionization efficiencies than Pu samples which were electrodeposited on to single, flat Re ribbons, similar to the procedure described by Perrin *et al.* (1985), but we did not rigorously test this alternative procedure.

To load the sample on to the beads at S.R.L., we first add 50–100 μl of 8 N HNO_3 to the bottom of a conical shaped Teflon beaker which contains the

evaporated and purified Pu sample (see following sections for the Pu chemical clean-up procedures). We then add two precleaned anion exchange beads (AG 1 × 2, 50–100 mesh, Bio-Rad Labs) to the Pu sample solution. The beads are left in the solution overnight, which allows ample time for the beads to quantitatively remove Pu from solution. The beads are then picked out of the nitric acid solution with a tungsten needle under a low powered microscope and placed into the center of a prepared filament trough. Once both beads have been loaded, a drop of dilute collodion solution is used to secure the beads in place on the ribbon. Two beads are used to ensure that if one bead fails to pick up the Pu for any reason, or is lost during handling, the second bead can still provide an adequate sample signal. Once loaded, the samples are placed into a vacuum chamber, where they undergo a preparatory heating procedure. The S.R.L. sample/preparatory procedure consists of slowly raising the current through the filaments (up to eight at a time) under vacuum ($p < 5 \times 10^{-6}$ torr) until a temperature of 1250°C is reached, as determined by an optical pyrometer. The purpose of this heating step is to slowly decompose the sample bead at relatively low temperatures, which is needed before the ionization of the Pu sample off the filament can occur. The filaments are kept at 1250°C for 45 min and then slowly brought back to room temperature. Care must be taken to ensure that the temperature on the filament is raised slowly, such that the bead or a fragment thereof does not fly off the ribbon. Careful monitoring of the chamber pressure can usually detect such a loss. After this step, the samples are ready for loading into the m.s.

Detection

The ion beam in the S.R.L. m.s. is measured in the pulse counting mode by an electron multiplier originally designed by Dietz (1965). The multiplier was constructed at S.R.L. and has virtually a 100% detection efficiency along with essentially zero background (three to four background counts per hour at a gain of 10^8) (Halverson, 1981). In the pulse counting mode, the current collected by the multiplier is passed through a pulse height discriminator, whereby only pulses above a certain threshold voltage are accepted as actual sample ion pulses. In this fashion, background noise signals are eliminated and, with proper design, more than 99% of all true sample pulses exceed the threshold voltage setting. The pulse counting mode of detection is critical for determining the exceedingly low abundances of Pu atoms present in our samples.

The standard filament temperature for optimal Pu ionization is 1350–1450°C. The filament is brought up to this temperature while monitoring the ^{242}Pu mass peak for an ion beam signal. The ion source is tuned at the ^{242}Pu mass peak in order to align the beam for maximum detection by the ion

multiplier. During a given sample run, the m.s. is programmed to scan the plutonium 239, 240, 242 and 243 mass peaks, including ±0·2 mass units around each peak (^{243}Pu is monitored to examine potential isobaric interferences from Fe and Re). ^{236}Pu and/or ^{241}Pu can also be examined if desired but, due to the abundance of ^{238}U in marine samples, ^{238}Pu cannot be measured with this technique. The optimal counting times at each mass peak are determined by the computer to minimize the variances of the estimated isotopic composition. Repeated mass scans (up to 64, depending upon the sample size and the ion beam strength) are made and the data are collected and reported as the atom percent of a given Pu isotope during the entire run. The reported atom percent error associated with each isotope is the uncertainty determined either from counting statistics from the square root of the total number of Pu ions detected at a given peak or by the variability in the atom percent values obtained between individual mass scans, whichever is greater. If no counts were detected at a given mass peak, then a maximum atom percent ratio is calculated assuming that one count had been detected at that mass during the run. No corrections in our data have been made for isotopic fractionation, since this effect has been shown to be rather small for the Pu isotopes ($<<1\%$) relative to the errors seen in our actual sample analyses (1–10%).

PREPARATION AND PURIFICATION OF MARINE SAMPLES FOR Pu ANALYSES BY M.S.

Prior to the m.s. analysis, Pu must be chemically separated and purified. The techniques used depend upon the initial sample type and are based primarily upon modifications of techniques used for the preparation and purification of marine samples for the detection of $^{239,240}Pu$ by alpha-counting (Wong, 1971; Livingston *et al.*, 1975).

Sample preparation

Prior to the Pu purification steps, all of the samples must be spiked and equilibrated with a ^{242}Pu tracer and brought up in a solution of 8 N HNO_3 before loading on to the first ion exchange column. These preparation procedures will be described below in some detail for each type of marine sample that has been analyzed.

Sediment preparation procedure

Typically, 1–10 g (dry weight) of oceanic sediments proved sufficient for the m.s. analysis of fallout ^{239}Pu and ^{240}Pu. An aliquot of dried sediment is placed into an acid-cleaned 500 ml beaker and 100 ml of 8 N HNO_3 (made with

reagent grade HNO_3 and deionized water) is carefully added along with 1 ml of our standard ^{242}Pu tracer. The tracer solution contains a known quantity of ^{242}Pu (0·2 pg) in dilute nitric acid, which has been weighed into an acid-cleaned plastic vial. The tracer is added to the sample using repeated (5 ×) rinses of the tracer vial with nitric acid to ensure a quantitative transfer. The beaker is then covered with a watchglass and heated gently to near boiling (≈80°C) and left overnight with occasional stirring. This acid/sediment slurry is subsequently filtered through an acid-cleaned glass fiber filter set-up followed by repeated rinsings of the original sample container and the sediment slurry with 8 N HNO_3. The filtrate is collected in a 500 ml beaker and is slowly evaporated down while the remaining solid residue is returned to the original beaker and re-leached in hot 8 N HNO_3 for an additional 6–8 hours. The sediment slurry is filtered a second time and this filtrate is added to the original sample solution. The combined filtrate is evaporated down until 50 ml of concentrated HNO_3 solution remains. An equal volume of deionized water is added to the sample, thus forming 100 ml of 8 N HNO_3 solution. One gram of $NaNO_2$ is added to the sample solution, which is heated slightly (10–15 min at 40°C) before the sample is ready to load on to the first ion exchange column. $NaNO_2$ serves to fix the Pu in the nitric acid solution in the +4 oxidation state, resulting in the formation of the negatively charged Pu–hexanitrate complex which is strongly adsorbed on to the anion exchange column (Milyukova *et al.*, 1969; Livingston *et al.*, 1975).

Sea water/pore water preparation procedure

The typical sample size we have been analyzing by m.s. for Pu in sea water is 3–5 liters, given sea water $^{239,240}Pu$ activities of $1–10 \times 10^{-3}$ Bq/m^3. For pore waters, the activity of Pu can be somewhat higher (Buesseler, 1986; Buesseler & Sholkovitz, 1987*a*) and the sample volume can therefore be reduced to the order of hundreds of milliliters. Since the total quantity of Pu in these samples is extremely small ($\simeq 10^{-15}$ g per sample), care must be taken to ensure that no Pu-bearing particles (i.e. natural sediments) enter the sample solution during handling. All of the purification procedures for the water samples are therefore performed in a clean-room facility and all glassware/Teflonware is stored in dilute acid baths prior to use.

Sea water and pore water samples are weighed into 2- or 6-liter beakers, followed by the addition of our ^{242}Pu spike. The sample and spike are equilibrated for 36–48 hours while being slowly stirred. The Pu sample is collected by a coprecipitation step which involves the addition of 1 ml of a pure Fe stock solution (20 mg ml^{-1} Fe in 1 N HNO_3) followed by the adjustment of the pH to 9–10 by the addition of concentrated reagent grade NH_4OH. The $Fe(OH)_3$ precipitates that form are stirred for 1–2 hours and

then allowed to settle overnight. Plutonium (and other actinides, metals, etc.) is carried by the Fe hydroxides. The sample supernate is carefully siphoned off the precipitate and the Fe precipitate slurry is collected in a 250 ml centrifuge tube with repeated rinsings of the sample beaker to quantitatively collect the Pu-bearing precipitates (using deionized water at pH = 8). The sample is then spun at 20 000 rpm for 30 min so that the overlying solution can simply be poured off the sample precipitates. The Fe precipitates are then dissolved in the centrifuge tube with ≃1–3 ml of concentrated HNO_3; 50 ml of 8 N HNO_3 is added to the sample along with 0·5 g of $NaNO_2$. The centrifuge tube is then heated in a 40°C waterbath for 10–15 min and the sample is now ready to run on to the prepared ion exchange column.

Sediment trap sample preparation procedure

5–10 mg samples of organic and inorganic settling particle debris that were collected by a sediment trap have been analyzed for Pu isotopes by m.s. The sediment trap samples are digested overnight under a heat lamp in a covered 30 ml Teflon beaker with the addition of a mixture of 1 ml each of reagent grade, concentrated HF, HCl, HNO_3 and our ^{242}Pu spike. The sample is taken to dryness and transferred to a 100 ml glass beaker with the addition of 3 ml of aqua regia. A second aqua regia rinse is used to ensure a complete transfer and the aqua regia solution is taken to dryness; 2 ml of concentrated nitric acid is added and the sample is evaporated to dryness. This nitric acid step is repeated a second time. After the final evaporation step, the sample is brought up in 50 ml of 8 N HNO_3, along with 0·5 g of $NaNO_2$. The sample is warmed to 40°C for 10–15 min to prepare the sample for the initial ion exchange column.

Coral sample preparation procedure

Coral samples ranging from 1 to 8 g dry weight were analyzed for Pu isotopes by m.s. Before sample digestion with the ^{242}Pu spike, a sequence of cleaning steps was performed on the coral samples. The cleaning involved first a 1–2 min rinse of the sample in 0·16 M HNO_3, followed by a 3–5 min sample rinse with a 50/50 mix of 30% H_2O_2 and 0·125 M NaOH. Each time between rinsing steps, the supernate was siphoned off the sample and discarded. Both of these cleaning steps were repeated a second time, but with warm solutions. After the final cleaning, the coral samples were rinsed twice with Milli-Q deionized water and dried overnight in a clean-air bench. The samples were then weighed, the ^{242}Pu spike was added and the sample was digested in 50 ml of 8 N HNO_3 and warmed overnight on a hotplate. The following day, 0·5 g of $NaNO_2$ was added to the sample, which was then kept at 40°C for 10–15 min before loading on to the first ion exchange column.

Plutonium purification by ion exchange

The purification of Pu from other actinides, metals and salts is accomplished by an ion exchange technique adapted from procedures described by Wong (1971), Livingston *et al.* (1975) and Perrin *et al.* (1985). A clean Pu source is essential for trace level Pu m.s. analyses, since the presence of other elements in the sample interferes not only with ionization and the general m.s. efficiency but can also cause isobaric interferences at the Pu mass peaks (Perrin *et al.*, 1985). The ion exchange procedures used are discussed below for each type of marine sample analysed. In general, the procedures are similar for all samples; however, the sediment samples require much more clean-up than do the water, sediment trap or coral samples.

Sediment ion exchange column no. 1

The first column used in the sediment purification procedure contains 20 ml of wet resin (AG1-X8, 50–100 mesh, Bio-Rad Labs) in a 1·5 cm i.d. ×30 cm column. The column is equipped with a 250 ml sample reservoir, glass wool plugs to contain the resin within the column, a stop-cock to control the flow rate and a 'goose neck' exit tube such that the resin cannot run dry if left unattended (see Fig. 1(a)). The column is preconditioned with 80 ml of concentrated HNO_3 followed by 100 ml of an 8 N HNO_3 solution to which 1 g of $NaNO_2$ has been added (the flow rate is kept at approximately 2 ml per minute). All of the solutions used in this and the second sediment column are made up from reagent grade acids and deionized water.

The sample is added to the column reservoir and allowed to flow through the column at a flow rate of 1 ml/min. The sample beaker is rinsed with 8 N HNO_3 and these washings—along with an additional 250 ml of 8 N HNO_3—are passed through the column (this step removes much of the Fe and U from the sample, which pass through the column under these conditions). Next, 150 ml of concentrated HCl are passed through the column at a fast flow rate (2–4 ml min^{-1}) which serves primarily to elute Th off the column. The Pu fraction is then collected by passing a solution of 150 ml concentrated HCl with 7·5 ml of 1 N NH_4I through the column at a flow rate of 1 ml min^{-1}. The NH_4I reduces the Pu to the +3 oxidation state, which is no longer adsorbed to the column and is thereby eluted. The eluted Pu fraction is collected in a 250 ml beaker and evaporated to dryness, using repeated treatments with aqua regia (2 × using 1 ml of aqua regia) to destroy the remaining NH_4I, followed by evaporating to dryness in the presence of HNO_3 (3 × using 2 ml of HNO_3) to return the sample to the nitric acid form.

Sediment column no. 2

The second ion exchange column used in the sediment procedure is similar to the first except that the volumes of acid and resin have now been greatly

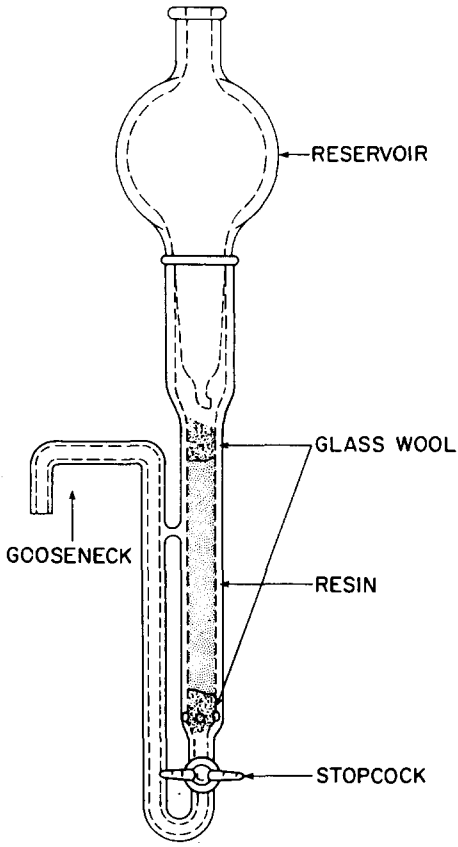

Fig. 1(a). 'Goose-neck' ion exchange column.

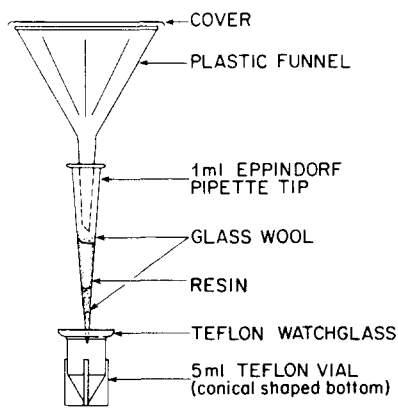

Fig. 1(b). 1 ml final ion exchange column.

reduced. The eluted Pu sample from the previous column is brought up in 5 ml of 8 N HNO_3 and 0·02 g of $NaNO_2$ is added with slight heating. The ion exchange column is made with 2 ml of resin (AG1-X8, 100–200 mesh, Bio-Rad Labs) in a glass column similar to the previous column in design, but with a 1·0 cm i.d. ×2 cm height. The sample is loaded on to the column with a glass pipette (acid-cleaned) in order to ensure that no sample solution is lost. Once loaded on to the column, the flow rate is maintained at roughly 1 ml min^{-1}. The sample is followed by 10 ml of 8 N HNO_3 which is used to rinse the beaker, followed by 20 ml of 8 N HNO_3 as a general column wash. After the nitric acid is eluted, 25 ml of concentrated HCl is passed through the column. Finally, the Pu is collected in a 50 ml beaker by passing a solution made up of 1·5 ml of 1 N NH_4I in 30 ml of concentrated HCl through the column at a flow rate of 1 ml min^{-1}.

This final Pu eluate is evaporated to dryness and, as with the first column, the NH_4I is destroyed by the addition of aqua regia (2 ×), between repeated

evaporations to dryness. The sample is finally brought to dryness (2 ×) with the addition of 1 ml of concentrated HCl.

Sediment column no. 3

The final Pu ion exchange column is similar for all samples and serves to achieve the added clean-up necessary for trace level Pu analysis by m.s. The column work is performed in a separate positive pressure clean-room, where the room air is continuously filtered through a large HEPA filter clean-air bench. All of the acids used in these steps are high purity grade to ensure that the final Pu eluate is free from any interfering contaminants (Seastar double sub-boiling distilled concentrated HNO_3 and HCl; EM Reagents 'Suprapur' high purity 47% HBr). The glassware/Teflonware is all hot acid leached (4 N HCl) and stored in 1 N HCl baths prior to use. The water which is used is distilled and deionized through a Millipore Milli-Q© water purification system. The following procedures are based on those of Larsen & Oldham (1974) and Perrin *et al.* (1985).

The final column is prepared in an acid-cleaned, disposable 1 ml Eppindorf pipette tip (see Fig. 1(b)). A plug of hot acid-leached and deionized water-rinsed glass wool is pressed into the tip of the column. The resin used is AGMP-1, 20–50 mesh (Bio-Rad Labs), which has been hot acid (4 N HCl)-leached and repeatedly rinsed with the deionized water and stored as a slurry in deionized water. The resin slurry is added to the column with a disposable plastic pipette such that a resin bed volume of 1 ml is obtained (2·5 cm height). A second glass wool plug is placed on top of the column and a 10 ml plastic funnel is pushed into the column top to serve as the sample and rinse solution reservoir. This reservoir is covered by a plastic top. The column is preconditioned with 2–3 ml of the HCl/H_2O_2 solution and the column flow rate is controlled simply by the column design, in particular by the density and packing of the initial glass wool plug.

The sample from the previous column is brought-up in 1 ml of freshly prepared HCl/H_2O_2 solution (10 ml concentrated HCl with one drop 30% H_2O_2 added). The sample is warmed slightly (≈40°C) for 60 min before loading on to the column with a plastic, disposable 3 ml pipette. This is followed by 2 ml of the HCl/H_2O_2 solution, which is used to rinse the original sample container before adding the solution to the reservoir. The HCl solution is followed by a 2 ml wash of 8 N HNO_3. Pu is eluted with 3 ml of concentrated HBr, which is collected directly in a 5 ml screw top, conical shaped Teflon vial. The vial is covered by a Teflon cover which permits the column tip to reach just inside the vial (see Fig. 1(b)). Once the HBr eluant is collected, the sample is placed under a heat lamp and the HBr solution is evaporated. When only a few drops of the HBr solution remain, six to eight

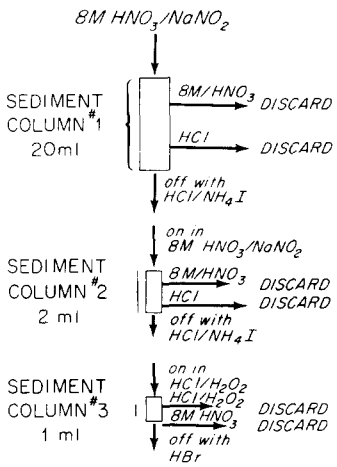

Fig. 2(a). Summary of ion exchange procedures for marine sediment samples.

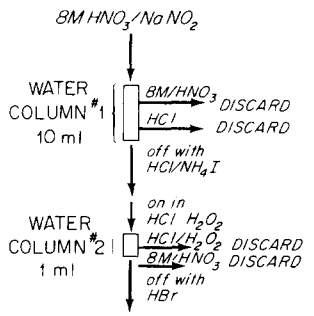

Fig. 2(b). Summary of ion exchange procedures for sea water, pore water, sediment trap and coral samples.

drops of concentrated HNO_3 are added to destroy any traces of HBr. The solution is evaporated to dryness, sealed with the threaded Teflon top and is now ready to be transported to the m.s. facility for loading and analysis. A summary of the sediment ion exchange purification procedures is provided in Fig. 2(a). The total recovery of Pu from the sediment during preparation and purification procedures averages between 70 and 80% as determined by a ^{242}Pu spike.

Sea water, pore water, sediment trap and coral sample column no. 1

The first ion exchange column for these samples is designed similarly to the initial sediment column except that the resin bed volume has been reduced to 10 ml. We use 10 ml of wet resin (AG1-X8, 50–100 mesh, Bio-Rad Labs) in a 1·0 i.d. ×20 cm tall 'goose-neck' column equipped with a 125 ml sample reservoir and a stop-cock to adjust the flow rate. The column is preconditioned with 50 ml of 8 N HNO_3 to which 0·5 g of $NaNO_2$ has been added (flow rate is 2 ml min^{-1}). All of the acids used in this column are reagent grade and, as required, are diluted with Milli-Q deionized water.

The sample is poured into the column reservoir and passed through the column at a flow rate of 1 ml min^{-1}. This is followed by three 5 ml 8 N HNO_3 rinses of the original sample centrifuge tube container and then a 150 ml column wash with 8 N HNO_3 at a flow of 1 ml min^{-1}. Next, 150 ml of concentrated HCl is passed through at a faster flow rate of 2 ml min^{-1}. The

Pu fraction is then eluted at a flow rate of 1 ml min^{-1} with 75 ml of concentrated HCl to which 6 ml of 1 N NH_4I solution has been added. This Pu fraction is collected in a 100 ml beaker and evaporated slowly to dryness. Two treatments with 1 ml of aqua regia are used to destroy the remaining NH_4I. The sample is prepared for the following column by evaporating the solution to dryness (3 ×) with the addition of 1–2 ml of concentrated HCl.

Sea water, pore water, sediment trap and coral sample column no. 2
Only two clean-up columns are used for these samples, the second ion exchange column being identical to the final sediment column no. 3 described previously (i.e. a 1 ml AGMP resin column; sample on as concentrated HCl/H_2O_2, off with HBr and into 5 ml Teflon vials with evaporation to dryness). A summary of the water, sediment trap and coral sample ion exchange procedures is given in Fig. 2(b). The total recovery of Pu from the water, sediment trap and coral samples during all preparation and clean-up procedures averages between 75 and 90% as determined by a ^{242}Pu spike.

RESULTS AND DISCUSSION

^{242}Pu tracer

The ^{242}Pu tracer used in this study was prepared in 1 N HNO_3 (made from Seastar double sub-boiling distilled HNO_3 and Milli-Q water) from a dilution of the NBS ^{242}Pu standard 4334-B. This standard has been routinely used in our labs as a yield monitor for Pu determinations by alpha-counting. It is important to check the blank values for all the Pu isotopes in our standard ^{242}Pu spike. Table 1 shows the results of two separate m.s. analyses of this spike. The ^{239}Pu and ^{240}Pu concentrations are so low that only an upper limit on the atom percent of these isotopes in the spike can be calculated assuming that one count of ^{239}Pu or ^{240}Pu was detected in the ^{242}Pu spike (see Table 1). We conclude that our ^{242}Pu spike is indeed free of any other Pu isotope contaminants.

The concentration of the ^{242}Pu m.s. standard was checked by intercalibration with a known quantity of a ^{239}Pu spike provided by the E.P.A. Labs in Las Vegas, Nevada, USA. Two samples consisting of 200 ml of our ^{242}Pu standard solution ($\simeq 7 \times 10^{-3}$ Bq ^{242}Pu each) were spiked with 7×10^{-3} Bq of the EPA ^{239}Pu solution and alpha-counted. Also, an aliquot of one of these samples (1/100th of the sample by volume) was analyzed directly by the S.R.L. m.s. to obtain an atom ratio of $^{239}Pu/^{242}Pu$ as well. The ^{242}Pu concentration of our spike is determined assuming that the quantity of

TABLE 1

Plutonium Isotopic Ratios by Mass Spectrometry in ^{242}Pu Spike and in Marine Sample Blanks

Sample	*Total counts*	*^{242}Pu atom %*	*Error*[a]	*^{239}Pu atom %*	*Error*[a]	*^{240}Pu atom %*	*Error*[a]	*^{239}Pu 10^{-15} g/sample*
^{242}Pu spike	6·9E + 05	99·993	0·267	0·000 7[b]	0·000 7	0·000 7[b]	0·000 7	
^{242}Pu spike	3·0E + 05	99·994	0·582	0·001 1[b]	0·001 3	0·001 1[b]	0·001 1	
Blank: pore water	3·0E + 05	99·967	0·572	0·025	0·005	0·008	0·003	0·061
Blank: pore water	2·5E + 05	99·967	0·639	0·026	0·006	0·007	0·004	0·064
Blank: pore water	2·6E + 05	99·909	0·631	0·032	0·008	0·035	0·006	0·080
Blank: pore water	2·0E + 05	99·936	0·707	0·025	0·007	0·009	0·003	0·062
Blank: sea water	2·1E + 05	99·957	2·067	0·030	0·007	0·013	0·003	0·074
Blank: sediment	5·5E + 05	99·459	1·286	0·431 6	0·021 1	0·109 8	0·005 53	1·054
Blank: sediment	3·0E + 05	99·489	1·755	0·402 3	0·025 1	0·108 7	0·009 3	0·999
Blank: sediment	4·9E + 04	99·772	4·298	0·174 5	0·033 0	0·052 9	0·017 0	0·430

[a]The reported error is the uncertainty calculated from the square root of the total number of m.s. counts of a given isotope or from the difference amongst atom percent values between individual mass scans, whichever is larger.

[b]These atom percent values are maximum estimates, since they are calculated assuming that one count of ^{239}Pu or ^{240}Pu was detected. In fact, no counts were detected during these runs.

added ^{239}Pu is precisely known. The results of the $^{239}Pu/^{242}Pu$ ratios determined by alpha-counting and by m.s. agree within the counting precision (±2·7% for alpha-counting and ±1·6% for m.s.). The calibrated ^{242}Pu concentration of our spike was determined, from these three analyses, to be 0·239 ± 0·003 pg $^{242}Pu\ g^{-1}$ solution. In practice, 1 g aliquots of this ^{242}Pu tracer solution are weighed into acid-cleaned vials and used for isotope dilution m.s. determinations of fallout ^{239}Pu and ^{240}Pu concentrations in our samples.

Blanks

Procedural blanks for the m.s. technique are given in Table 1. These blanks are determined by running a ^{242}Pu spike through all of the associated preparation and purification procedures described previously for the sediment and water samples. The sediment sample blank is significantly higher than that of the water samples, which is likely due to the additional handling and reagents needed in the sediment analytical technique. A blank correction of $0{\cdot}8 \times 10^{-15}$ g ^{239}Pu/sample has been applied to our sediment data. This blank value represents a correction of <1% of the total mass of ^{239}Pu in most of these sediment samples. The blanks for the sea water and pore water samples are identical due to the similar handling procedures used on these samples. The observed blank for these samples averaged $0{\cdot}07 \times 10^{-15}$ g ^{239}Pu/sample (see Table 1). Though a sediment trap or coral blank was not directly measured, these samples have been corrected by this same Pu water procedural blank, due to the similarity in handling procedures between these sample types.

Sample results

Results for an assortment of marine samples are given as atom percent values, $^{240}Pu/^{239}Pu$ ratios and Pu concentrations in Table 2. Complete results and their interpretations are presented elsewhere (Buesseler, 1986; Buesseler & Sholkovitz, 1987*a*, *b*). The Pu determinations by m.s. agree well with alpha-counting determinations of Pu on larger quantities of the same sample (see Table 2). Also, repeated analyses of the same sea water sample by m.s. have provided consistent Pu ratios and concentrations within the analytical precision (see 'Sargasso Sea surf.' sample in Table 2). Intercalibration exercises have been run between the Savannah River Laboratory and other m.s. facilities at Los Alamos and Scripps and provide excellent agreement between labs in the determination of $^{240}Pu/^{239}Pu$ ratios (Koide *et al.*, 1985).

In practice, to achieve a total analytical error at less than 10% on the

TABLE 2

Selected Plutonium Analyses by Mass Spectrometry (m.s.) in North Atlantic Marine Samples (with comparisons to alpha-counting)

				Plutonium					*m.s. detection*			*Alpha-detection*	
Sample	^{242}Pu *atom %*	^{239}Pu *atom %*	^{240}Pu *atom %*	*Ratio 239/242*	*± Error 239/242*	*Ratio 240/239*	*± Error 240/239*	*Sample weight (g)*	*Pu dpm sample^{-1}*	*Sample $^{239,240}Pu$*		*Sample weight (g)*	$^{239,240}Pu$
Sediments										(dpm kg^{-1})	(Bq kg^{-1})		(dpm kg^{-1})
SEEP LVA1:0–1·5 cm	92·667	6·224	1·088 4	0·067 2	0·001 6	0·175	0·008	0·30	0·034 5	114·76 ± 5·90	1·91	15	107·1 ± 4·9
SEEP LVE1A:0–1 cm	21·102	68·125	10·769 9	3·228 4	0·018 7	0·158	0·002	2·80	0·167 8	59·92 ± 0·78	0·999	15	62·7 ± 3·5
SEEP LVE2A:2–3 cm	97·571	2·127	0·302 0	0·021 8	0·000 5	0·142	0·009	0·30	0·010 7	35·49 ± 2·39	0·592	15	36·2 ± 2·2
SEEP LVE8:14–16 cm	99·951	0·042	0·006 7	0·000 4	0·000 03	0·159	0·029	0·30	0·000 2	0·70 ± 0·14	0·012	15	0·8 ± 0·4
SEEP LVF1A:0–1 cm	98·217	1·513	0·270 7	0·015 4	0·000 3	0·179	0·005	0·30	0·007 9	26·23 ± 0·89	0·437	15	27·4 ± 2·1
Pore water										(dpm 100 kg^{-1})	(Bq m^{-3})		
SEEP LVE1:0–2 cm	94·094	4·997	0·893 4	0·053 1	0·000 6	0·179	0·007	515	0·002 9	0·567 ± 0·007	0·095		
SEEP LVE2:2–4 cm	98·659	1·115	0·205 1	0·011 3	0·001 1	0·184	0·044	502	0·000 6	0·122 ± 0·012	0·020		
SEEP LVF1:0–2 cm	97·788	1·859	0·348 9	0·019 0	0·000 4	0·188	0·007	574	0·001 0	0·181 ± 0·004	0·030		
Sediment trap material										(dpm g^{-1})	(Bq mg^{-1})		
SEEP no. 4 1200 m	97·541	2·078	0·372 2	0·021 3	0·000 5	0·179	0·008	0·004 7	0·001 1	0·244 ± 0·012	4·07		
EN CMME-4 3985 m	93·764	5·262	0·945 5	0·056 1	0·002 5	0·180	0·013	0·008 6	0·003 1	0·355 ± 0·030	5·92		
Sea water										(dpm 100 kg^{-1})	(Bq m^{-3})		
Sargasso Sea surf.	99·801	0·163	0·029 5	0·001 6	0·000 03	0·181	0·011	1 300	0·001 8	0·138 ± 0·009	0·023	55 000	0·13 ± 0·03
Sargasso Sea surf.	99·825	0·148	0·026 6	0·001 5	0·000 045	0·180	0·011	1 400	0·001 8	0·129 ± 0·009	0·022	55 000	0·13 ± 0·03
SEEP STA-D:1700 m	99·763	0·193 7	0·040 9	0·001 9	0·000 1	0·211	0·018	1 000	0·001 0	0·099 ± 0·009	0·017	55 000	0·10 ± 0·01
SEEP STA-F:454 m	99·885	0·095 8	0·018 4	0·000 96	0·000 025	0·192	0·010	1 000	0·001 3	0·124 ± 0·007	0·021	55 000	0·13 ± 0·01
Coral samples										(dpm mg^{-1})	(Bq mg^{-1})		
Pacific 1957/58	57·466	34·391	8·214	0·597	0·087	0·239	0·035	2·76	0·037 6	13·63 ± 2·82	0·227		
Pacific 1963/64	40·477	49·863	9·660	1·232	0·011	0·194	0·002	7·85	0·070 3	8·95 ± 0·12	0·149		

$^{240}Pu/^{239}Pu$ atom ratio and on the $^{239,240}Pu$ activity determinations, a sample size of $\approx 0{\cdot}5\text{–}1 \times 10^{-3}$ dpm total Pu (i.e., ^{239}Pu plus ^{240}Pu) is needed. This is equivalent to $0{\cdot}85\text{–}1{\cdot}7 \times 10^{-5}$ Bq $^{239,240}Pu$ or $2\text{–}4 \times 10^{-15}$ g at ^{239}Pu per sample assuming the global average fallout $^{240}Pu/^{239}Pu$ atom ratio of 0·18 (Perkins & Thomas, 1980; Buesseler & Sholkovitz, 1987*b*).

As far as the analysis of environmental marine samples is concerned, it must be remembered that the Pu concentration range spans seven orders-of-magnitude on a weight basis, when one is dealing with sediment trap, sediment, pore water and sea water samples (see insert, Fig. 3). If typical collected sample weights for each of these sample types are compared to the range of Pu activities found, several factors become clear (Fig. 3). For all of

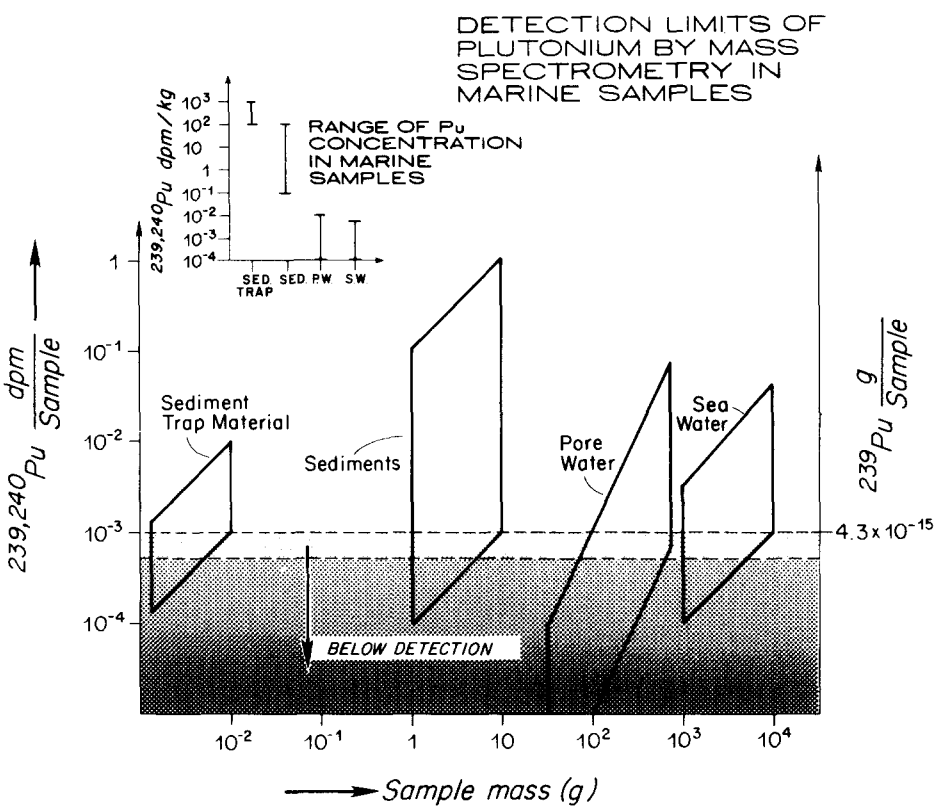

Fig. 3. A summary of the range of fallout Pu activities found in typical marine samples relative to detection by m.s. The insert shows the range of $^{239,240}Pu$ activities found in the marine environment. These Pu concentration ranges are multiplied by standard sample collection masses to arrive at the expected $^{239,240}Pu$ content per sample type. This is then compared to the limit of determination (with a 10% error) found for $^{239,240}Pu$ in this study. 10^{-3} dpm $^{239,240}Pu = 1{\cdot}7 \times 10^{-5}$ Bq $^{239,240}Pu = 4{\cdot}3 \times 10^{-15}$ g ^{239}Pu (assuming a $^{240}Pu/^{239}Pu$ atom ratio of 0·18). See Section 'Sample results' for discussion.

these sample types, some combination of relatively high activity and/or large sample mass can provide ample Pu above the detection limit of this m.s. technique. This is easiest to obtain for sediments, where most samples have considerable activity and where multigram sampling is common and straightforward. It must be remembered, however, that prebomb samples of any type should have essentially blank signals. The pore water samples prove the most difficult to analyze since Pu activities are extremely low and since the volumes of sample that can be collected are rather small. The range in pore water sample mass used in Fig. 3 (50–900 g) is rather large, requiring considerable effort to collect given the available sampling techniques. Since the total Pu signal in marine sediments is often concentrated in the uppermost centimeters of a core, the pore water Pu signal will only be above detection in relatively large samples from the core top. Sea water samples can be as low in Pu activity as the pore waters but here much larger water volumes can be easily collected.

In general, thermal ionization m.s. provides a number of advantages for environmental studies of Pu. The increased sensitivity of the m.s. detection technique allows for the determination of Pu on liter quantities of sea water in contrast to the 50–100 liter water samples used for alpha-counting analyses. These smaller volumes are much more practical to obtain and provide real savings in terms of the costs and effort needed not only in sampling but also in the sample preparation and purification steps. In addition, the gain in isotopic information which the m.s. provides has been shown to be a valuable indicator of the source(s) of fallout Pu at a given site (Scott *et al.*, 1983; Koide *et al.*, 1985; Buesseler & Sholkovitz, 1985; Buesseler, 1986; Buesseler & Sholkovitz, 1987*b*). The isotopic ratio of $^{240}Pu/^{239}Pu$ can also potentially be used to trace the relative significance of reactor vs. fallout Pu at a given site or to trace releases of Pu in nuclear waste disposal operations.

CONCLUSIONS

1. Thermal ionization m.s. provides an extremely sensitive technique for the detection of Pu in marine samples. This technique is orders-of-magnitude more sensitive than alpha-counting detection techniques, which is a valuable feature in environmental studies where Pu concentrations are extremely small.
2. The chemical preparation and purification procedures for the analysis of Pu by m.s. are similar to those used for alpha-counting, with some additional attention needed to maintain clean sample conditions and low blanks.

3. The Savannah River Laboratory m.s. facility can analyze 8 Pu samples within a period of roughly 8 hours. This is considerably faster than the detection times needed for alpha-counting. The inherent problem with alpha-counting is that the long half-lives of alpha-decay for ^{239}Pu (24 390 years) and ^{240}Pu (6620 years) combined with the low abundances of these isotopes in the environment simply result in extremely few alpha-decay events during the course of a given counting interval.
4. The isotopic ratio of ^{240}Pu/^{239}Pu can be accurately determined by m.s. This can provide valuable additional information concerning the source of Pu in a given sample (Buesseler, 1986; Buesseler & Sholkovitz, 1986*b*).

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