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ISOLATION AND ALPHA-PARTICLE  
SPECTROMETRIC DETERMINATION OF  
 $^{238}\text{Pu}$  AND  $^{239,240}\text{Pu}$  IN SEDIMENTS

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MANAGEMENT PERSPECTIVE/IMPLICATIONS OF RESEARCH

The title radioisotopes may be released to the aquatic environment as a result of nuclear fuel reprocessing activities (such as those until 1972 at West Valley, NY) or as a result of nuclear weapons' testing or satellite burnup in the atmosphere. In order to test the former possibility a simple radiochemical technique was required to rapidly and satisfactorily analyze a large number of sediment samples collected from Lake Ontario at the mouth of Niagara River for these radionuclides. The present article thus describes the method developed for this purpose. The method employs a simple sample extraction with nitric acid prior to isolation of radioisotopes on an anion exchange column. A novel lanthanum fluoride coprecipitation technique step eliminates the expensive, time-consuming electrodeposition technique for final source preparation for spectrometric assay. In addition to cost effectiveness for chemical processing, the described procedure also permits isolation and subsequent determination of six thorium and uranium isotopes. With the development of these procedures we now have the capability to analyze environmental samples containing extremely small amounts of various plutonium, thorium and uranium isotopes.

SÉPARATION ET ANALYSE SPECTROMÉTRIQUE (PARTICULES ALPHA)  
DES ISOTOPES Pu <sup>238</sup>, <sup>239</sup>, <sup>240</sup> DANS LES SÉDIMENTS

par

S.R. Joshi

PERSPECTIVE-GESTION - RÉSULTATS DES RECHERCHES

Les radio-isotopes peuvent être diffusés dans des milieux aquatiques à la suite d'activités de retraitement du combustible nucléaire (comme celles réalisées jusqu'en 1972, à West Valley, N.Y.) ou à la suite d'essais d'armes nucléaires ou de combustion de satellites dans l'atmosphère. Afin d'évaluer la dernière possibilité, il a fallu concevoir une technique radiochimique simple pour analyser rapidement et convenablement de nombreux échantillons de sédiments prélevés dans le lac Ontario à l'embouchure de la rivière Niagara pour déterminer la présence des radio-nucléides en question. Par conséquent, le présent article décrit la méthode conçue à cette fin. Il s'agit d'une simple technique d'extraction d'échantillons au moyen d'acide nitrique avant la séparation des radio-isotopes dans une colonne d'échangeur d'anions. Une nouvelle technique de co-précipitation du fluorure de lanthane remplace la technique d'électro-déposition onéreuse et lente qui servait à préparer la source aux fins de l'analyse spectrométrique. En plus d'être rentable en ce qui a trait au traitement chimique, la méthode décrite permet également de séparer, puis de déterminer six isotopes de thorium et d'uranium. Grâce à cette nouvelle méthode, il est maintenant possible d'analyser des échantillons environnementaux contenant des quantités extrêmement faibles de divers isotopes de plutonium, de thorium et d'uranium.

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EXECUTIVE SUMMARY

The title radioisotopes are introduced into the environment as a result of nuclear weapons' testing ( $\text{Pu-}^{239,240}$ ) or due to satellite burnup in the atmosphere ( $\text{Pu-}^{238}$ ). However, the possibility exists that all these radioisotopes may also reach aquatic environment due to nuclear fuel reprocessing activities such as those carried out until 1972 in West Valley, NY. In order to assess the significance of the latter, a technique was required to analyze sediment cores (from Lake Ontario at the mouth of Niagara River) for the presence of these radioisotopes. The present article describes the simple method developed for this purpose. The technique employs simple extraction with nitric acid prior to ion-exchange separation. A novellanthanum fluoride coprecipitation step eliminates conventional, expensive and time-consuming electrodeposition technique. In addition the described procedures also permit simultaneous determination of six thorium and uranium isotopes.

RÉSUMÉ ADMINISTRATIF

Les radio-isotopes en question pénètrent l'environnement à la suite d'essais d'armes nucléaires ( $\text{Pu }^{239, 240}$ ) ou de combustion de satellites dans l'atmosphère ( $\text{Pu }^{238}$ ). Cependant, il se peut que tous ces radio-isotopes atteignent également des milieux aquatiques à la suite d'activités de retraitement du combustible nucléaire, comme celles réalisées jusqu'en 1972, à West Valley (N.Y.). Afin d'évaluer l'importance de ces dernières, il a fallu concevoir une technique pour analyser des carottes de sédiments (prélevées dans le lac Ontario à l'embouchure de la rivière à Niagara) pour déterminer la présence de radio-isotopes. Le présent article décrit la méthode simple conçue à cette fin. Il s'agit d'une technique d'extraction simple, au moyen d'acide nitrique, avant la séparation qui s'effectue par échange d'ions. Une nouvelle technique de co-précipitation du fluorure de lanthane remplace la technique d'électrodéposition conventionnelle, onéreuse et lente. De plus, la méthode décrite permet également de déterminer simultanément six isotopes de thorium et d'uranium.

A simple method is described for the isolation and determination of plutonium isotopes in sediments. The method involves leaching of sample with nitric acid and subsequent separation of plutonium on an anion-exchange column. Major matrix elements and several potential radiochemical interferences are removed during 8M  $\text{HNO}_3$  sample loading on the column. Thorium is removed by thorough washing with 10 M  $\text{HCl}$ . Plutonium (IV) is eluted with 4M  $\text{HCl}$ . Source for alpha-particle spectrometry is prepared by  $\text{LaF}_3$  coprecipitation technique at which stage a complete separation from uranium (VI) is also achieved. The entire analytical procedure is completed in about two days.

On décrit une méthode simple pour séparer et analyser les isotopes du plutonium présents dans les sédiments. La méthode consiste à lessiver un échantillon au moyen d'acide nitrique, puis à séparer le plutonium dans une colonne d'échangeur d'anions. Les principaux éléments de la matrice et plusieurs interférences radiochimiques possibles sont éliminés au cours de la mise en place de l'échantillon de 8M  $\text{HNO}_3$  dans la colonne. Le thorium est enlevé au moyen d'un lavage complet au 10 M  $\text{HCl}$ . On procède à l'élution du plutonium (IV) par du 4M  $\text{HCl}$ . La source qui fera l'objet de spectrométrie d'émission de particules alpha est préparée par la co-précipitation du  $\text{LaF}_3$ , stade auquel les isotopes de plutonium se séparent entièrement de l'uranium (VI). L'analyse complète s'effectue en deux jours environ.

### Introduction

Of all the transuranium elements in the environment, plutonium has been studied most extensively and numerous procedures have been reported for its determination. All the reported procedures are necessarily based on wet chemistry since extremely low gamma-emission probabilities of various plutonium isotopes preclude direct determination by gamma-ray spectrometry. Excellent review articles have addressed the major approaches to developing analytical schemes and have illustrated the problems in measuring plutonium isotopes in environmental samples<sup>1,2</sup>.

Ongoing NWRI research projects require analyses of a large number of sediment samples for various radionuclides including <sup>238</sup>Pu and <sup>239,240</sup>Pu. Our major objective was to perform reliable plutonium analyses as rapidly and simply as possible with minimum use of complicated procedures and apparatus. Further, the technique must be adaptable in sequential analyses for other actinides when required. Procedures employing extraction with tri-n-octylphosphine oxide<sup>3</sup> (TOPO) and trilaurylamine<sup>4,5</sup> (TLA) were considered promising in effecting a quick separation of plutonium from matrix elements and other actinides. Of these the TOPO procedure proved to be quite messy and consistently yielded unsatisfactory results even when other variations of the technique<sup>6,7</sup> were applied. The liquid anion-exchange (TLA) procedure could not provide a complete separation of

plutonium from uranium and thorium. Our experience in using this procedure essentially parallels that of VESELSKY<sup>4</sup> in that the procedure removes only a major amount of thorium, but not all as has been claimed by SINGH et al.<sup>5</sup>. Replacement of TLA with other tertiary amines, including Alamine-336 and Adogen-364, did not improve the results either. The inability of this procedure to completely remove thorium interferes with the measurement of  $^{238}\text{Pu}$  whose 5.47 and 5.50 MeV alpha peaks are very closely flanked by alpha emissions from  $^{228}\text{Th}$  (5.34 and 5.43 MeV) and ingrown  $^{224}\text{Ra}$  (5.68 MeV).

In light of above results from preliminary investigations, it was decided to reevaluate the utility of the classic resin anion-exchange techniques for the isolation and radiochemical separation of plutonium with the view of simplifying elution steps using well-established anion-exchange properties of plutonium<sup>8</sup>, uranium<sup>9</sup> and thorium<sup>10</sup> in the nitrate and chloride systems. The present article thus describes a method for measuring plutonium in sediments based on these findings. The method provides much more consistently reliable separation of plutonium from thorium and uranium isotopes and does not require expensive extractants. In the past also, methods based on resin anion-exchange technique have yielded similarly consistent results when plutonium was eluted in the presence of a reducing agent<sup>11-13</sup>. A major argument against using column anion-exchange technique has been the time required to satisfactorily operate the column. The present method rectifies this situation to

some extent since the time-consuming electrodeposition step has been replaced by a lanthanum fluoride coprecipitation technique for the preparation of source for alpha-particle spectrometry<sup>14</sup>. The inclusion of this technique also ensures that plutonium is further separated from hexavalent uranium which stays in solution.

### Materials and Methods

#### Reagents and radiotracer

All the reagents used were of analytical grade and the solutions were prepared in distilled deionized water. All samples and solutions were stored in polyethylene bottles. High alpha-purity  $^{242}\text{Pu}$  was obtained from Oak Ridge National Laboratory, Oak Ridge, U.S.A. This radiotracer was preferred over  $^{236}\text{Pu}$  as it shows no ingrowth of daughters.  $^{236}\text{Pu}$ , on the other hand, requires periodic purification and standardization to remove  $^{232}\text{U}$  and  $^{228}\text{Th}$  daughters which otherwise interfere in the determination of  $^{238}\text{Pu}$ <sup>15</sup>.

#### Nuclear instrumentation

An EG&G Ortec silicon surface barrier detector (R-series) was used for alpha-particle spectrometry with a window of 600 mm<sup>2</sup>, a minimum sensitive thickness of 100  $\mu\text{m}$ , and a resolution of 23.9 keV



for an infinitely thin, 5.486 MeV  $^{241}\text{Am}$  source. Amplified and shaped pulses from the detector, mounted in a vacuum chamber, were analyzed on a Nuclear Data 66 pulse-height analyzer. Direct communication between ND 66 and 6620 units permitted an efficient handling and storage of data.

#### Column preparation

Pour 100 g of Dowex 1-X8 resin (100-200 mesh,  $\text{Cl}^-$  form; BioRad Laboratories, Richmond, CA., U.S.A.) into a 1-L beaker prior to addition of 500 mL of water. Stir the slurry for 5-10 min and, when the bulk of the resin has settled slowly, decant the water along with the fines. Repeat the washing 3-4 times and pour about 20 g of resin into a borosilicate column and wash with 10-12 column volumes of 2M NaOH and then with 10-12 column volumes of water. Convert the resin to the nitrate form by washing with 8M  $\text{HNO}_3$  until a silver nitrate test of the wash shows the absence of chloride. Replace the resin in the column by a new batch after four or five samples have been processed. Avoid prolonged storage of resin in high nitric acid concentrations as it promotes degradation.

#### Analytical procedure

Transfer the dried, powdered and weighed (usually about 100 g) sample to a platinum crucible and destroy organic matter by

heating the covered crucible in a muffle furnace for at least two hr. Carefully transfer the sample to a standard reflux unit using 8M  $\text{MNO}_3$  and 1 g of sodium nitrite to stabilize  $\text{Pu}^{4+}$  ion. Without stabilization disproportionation reactions occur and  $\text{Pu}^{4+}$  is converted to a mixture of several species. Add  $^{242}\text{Pu}$  tracer (30-40 mBq), soak the sample completely with 8M  $\text{MNO}_3$ , and reflux for 2-3 hr. Any excessive fuming may be controlled by dropwise addition of n-octanol. Filter hot through Whatman 42 paper. Retain the filtrate and leach the sample again using 8M  $\text{MNO}_3$ . Repeat the process once more and combine all three leached fractions. Cool to room temperature and then pass through the anion-exchange column at a flow rate of about 1 mL/min. Remove interfering elements by washing with three column volumes of 8M  $\text{HNO}_3$ . Remove thorium by washing the column with 12 column volumes of 10M  $\text{HCl}$ . Elute plutonium by washing with 3-4 column volumes of 4M  $\text{HCl}$ . Reduce the volume of the eluate without taking it to complete dryness and throughout ensuring that enough sodium bisulphite is present. Adjust the molarity of hydrochloric acid to about 0.1 M in a 50 mL sample placed in a Teflon FEP beaker. Prepare the source for alpha-particle spectrometry using  $\text{LaF}_3$  coprecipitation technique<sup>14</sup>. Accumulate spectrum until reasonable counting statistics are obtained and compute the  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  concentrations using  $^{242}\text{Pu}$  data.

### Results and Discussion

The key to an accurate measurement of sedimentary  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  by alpha-particle spectrometry is to obtain plutonium fraction free from major matrix components such as silica, iron, aluminium, etc. and other alpha-emitters. Excellent procedures<sup>16,17</sup> have been described to obtain high decontamination factors for plutonium from other alpha-emitters. Unfortunately, both procedures are best applied to samples considerably smaller than were required in our studies where only a few mBq/g of plutonium are present. Furthermore, both methods require a precise control over the oxidation state. The method based on extraction with bis (2-ethylexyl) phosphoric acid<sup>17</sup> also requires potentially hazardous operations with perchloric acid.

The most critical issue in measuring plutonium in sediments involves sample decomposition and ensuing exchange between tracer and other isotopes. In this context, the pros and cons of fusion and leaching procedures have been discussed extensively in the literature and it has been amply demonstrated that the surest method of solubilizing plutonium in samples of unknown thermal pretreatment and chemical composition is to use a fluoride-pyrosulphate fusion technique<sup>18</sup>. In practice, however, this fusion technique is applied only to very small samples which may not truly represent the populations from which they are taken. A larger sample would mitigate

this concern and leaching with a mineral acid should readily dissolve plutonium originating from global fallout or adsorbed from aqueous solutions<sup>4</sup>. Previous investigators have usually employed mixtures of mineral acids to solubilize plutonium. We have preferred to use nitric acid alone in order to simplify further analytical steps.

Following leaching or dissolution of a fusion cake, the analyst has two basic choices for isolating plutonium from major matrix elements. Thus, plutonium can be isolated by coprecipitation with ferric hydroxide, calcium oxalate, bismuth phosphate or a rare earth fluoride or by direct loading on the ion exchange column as a chloro or a nitrate complex. We investigated lanthanum fluoride coprecipitation technique<sup>14</sup> as it offers the advantage that bulk constituents such as iron are effectively removed by incorporating simple reductive steps. We got encouraging results but had to shelve this approach for several reasons. Firstly, the sheer volume of the solution of required acidity was intimidating. Secondly, the desired coprecipitation of U(VI), even after reduction with titanium chloride, was found to be very erratic. Thirdly, we found that the steps required to remove lanthanum and fluoride ions at a later stage would lengthen the procedure. It is worth noting that we could not get satisfactory results when extraction of plutonium, uranium and thorium into TOPO or a tertiary amine was attempted from nitric or hydrochloric acid solutions containing borate-complexed fluoride ion. In the second basic choice plutonium is generally absorbed as a

nitrate complex<sup>8</sup>. Some researchers prefer to absorb the chloro complex to take advantage of faster retention of this complex<sup>19</sup>. However, the large amount of iron present in the sediments not only promotes unnecessary competing exchange processes but also requires larger resin volumes since the amount of iron present in a typical 100-g sediment sample exceeds the breakthrough capacity of 20-mL resin bed by a factor of about 4. We, therefore, chose to load the nitrate complex. Furthermore, this step does not require any additional chemical manipulation and, more importantly, major matrix elements such as iron, aluminium and silica, the alkaline earths which include radium isotopes,  $^{241}\text{Am}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Bi}$  are not retained on the nitrate column. In addition, leaching with  $\text{HNO}_3$  also destroys any residual organic matter in the sample.

Elution with 10M HCl selectively removes thorium but not  $^{210}\text{Po}$ ,  $\text{Pu(IV)}$  and  $\text{U(VI)}$ . We have earlier<sup>20</sup> confirmed this aspect of the separation scheme. While elution with three or four column volumes removes most of the thorium, we have observed that as many as 12 column volumes are necessary to completely remove thorium which otherwise interferes in the subsequent alpha spectrometric assays. Plutonium is generally eluted with hydrochloric acid containing a reducing agent. In our experience, addition of reducing agent to column either disrupts the physical integrity (and perhaps also the retention characteristics) of the column ( $\text{NaHSO}_3$ ) or introduces additional ions which subsequently have to be removed ( $\text{NH}_4^+$  in case of

NH<sub>4</sub>I). Since we wished to keep the procedure as simple as possible, plutonium was eluted as Pu(IV) using 4M HCl. At this molarity of HCl, the distribution coefficient of Pu(IV) is about 0.6 while that of U(VI) is about 200. Despite the fact that the distribution coefficient of U(VI) has been significantly lowered from a high of about 1000 (10M HCl), a significant amount of U(VI) is still retained on the column so that a subsequent elution, with say 1M HCl, should permit an acceptable recovery of U(VI) as well. Thus, the obvious advantage of using this procedure is that it is possible to elute Th(IV), Pu(IV) and U(VI) using only single acid of varying molarities.

The final step in the chemical procedure avoids the time-consuming electrodeposition technique. Electrodeposition often requires precise control over pH which is often adjusted by use of an alkali. Furthermore, as Sill<sup>1</sup> has correctly pointed out, the addition of alkali promotes local formation of rather insoluble plutonium hydroxides and can also result in formation of impure heavy metal hydroxide carriers. This results in substantially reduced yields of electrodeposition and spectral degradation. The likelihood of electrodeposition apparatus contamination due to repeated use may further aggravate the problems encountered in conventional electrodeposition techniques. Coprecipitation with LaF<sub>3</sub> is free from these problems as the procedure is entirely carried out in an acidic medium without recourse to elaborate equipment. Under the described conditions only plutonium is coprecipitated while U(VI) effectively

stays in solution. This feature permits a simple separation of U(VI) present in the plutonium fraction from the anion-exchange step. The alpha-particle spectrum of plutonium fraction isolated from a Lake Ontario sediment core section obtained using the described method is shown in Figure 1. The alpha peaks from  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$  and  $^{242}\text{Pu}$  are well resolved and the spectrum is free from contributions due to various thorium and uranium isotopes.

The described method has been in use at NWRI since 1983 and has worked equally well with three different analysts. The entire analytical procedure is completed in about two days, excluding counting time, on a single sample. This time period is, however, substantially reduced when several samples are analyzed simultaneously. The method does not require any prohibitively expensive special reagents and equipment.

#### Acknowledgements

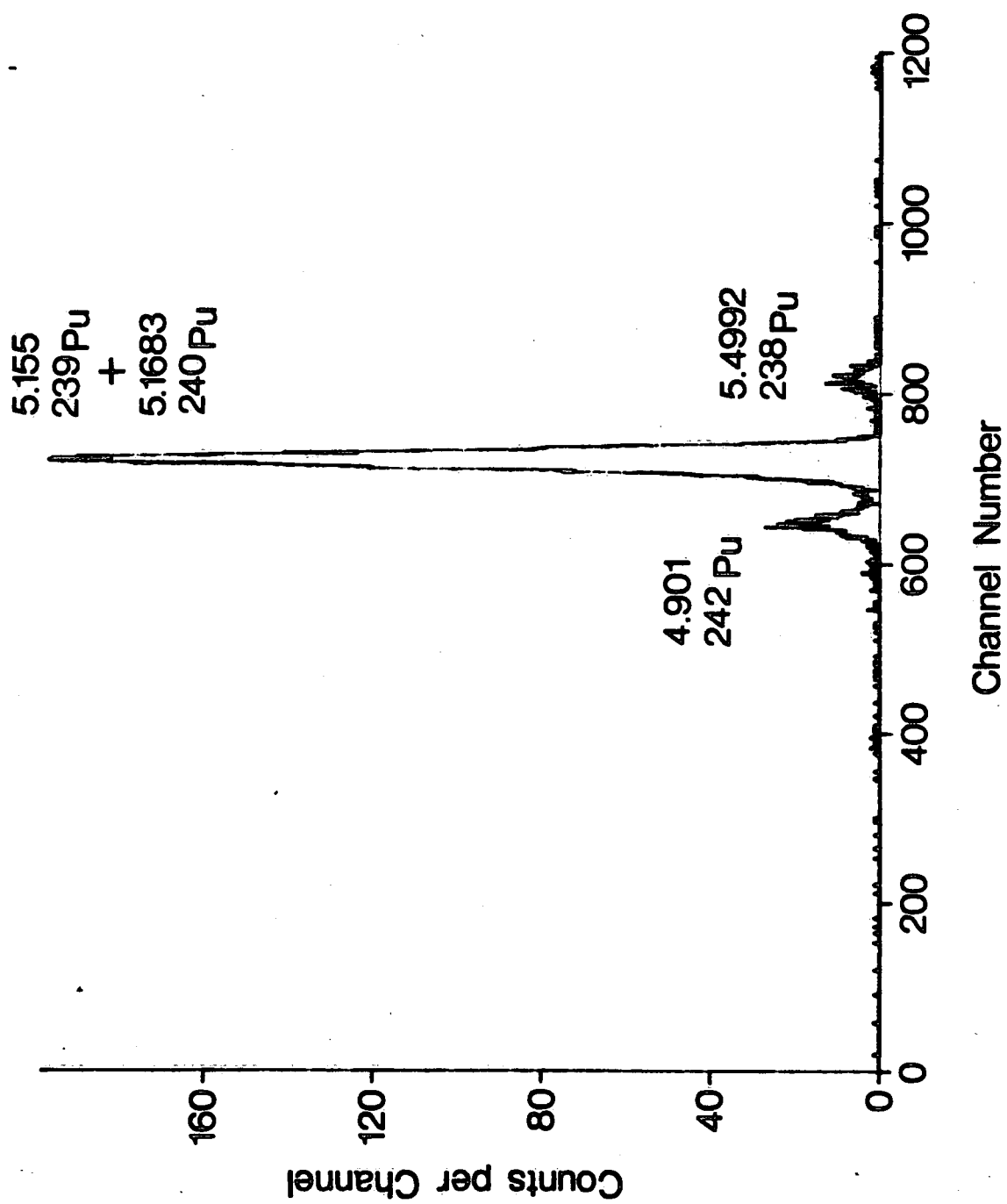
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**FIGURE CAPTIONS**

Figure 1 Alpha-particle spectrum of plutonium fraction isolated from a Lake Ontario sediment sample. Energies in MeV.