

Determination of americium-241 in sediments by gamma spectroscopy *

MIRJANA DJ. RISTIĆ^{1**}, SANDRO DEGETTO² and TEODOR AST^{1***}

¹Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Yugoslavia and ²Istituto di Chimica e Tecnologia del CNR, Corso Stati Uniti 4, I 35020 Padova, Italy

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A radiochemical method is given for the determination of Am-241 from the global fallout in sediments. The concept of a concentration step to separate Am-241 from the bulk of the sample (1–2 kg wet) by coprecipitation followed by low energy gamma spectroscopy was investigated. A series of experiments with tracer added was performed to measure the recovery of americium by coprecipitation. Also, a number of real samples without tracer were examined and the conditions for the optimum separation are given. The applied gamma method and the conventional, accurate, but tedious, alpha technique via ²⁴³Am, which is usually applied for the determination of Am-241, agreed mostly within 10 %.

Keywords: americium-241, low energy gamma spectroscopy, sediments, preconcentration.

INTRODUCTION

Americium-241 is a transuranic element of the nuclear fuel cycle. Possible accidental release of this radionuclide into the biosphere by installations of the nuclear industry may have serious consequences, because it is a long-lived alpha emitter. However, it is present in the environment in very low concentration, as a result of the global fallout from atmospheric nuclear weapon testing.

As well as its decay by alpha emission (100 %), Am-241 (half life 433 years) also emits a 59.5 keV gamma ray with an abundance of 36 %. If an efficient low energy gamma ray detector is used, then assuming small source dimensions, a sensitive limit of detection can be achieved.¹ Thus, for certain samples or measurements, the extremely lengthy and demanding radiochemical separation, electroplating of a thin source and alpha spectroscopy required in the traditional methods^{2–4} can be avoided.

However, gamma ray spectroscopy is capable of providing a general sensitivity of about 0.5 Bq/kg for Am-241, while the actual concentration of fallout Am-241

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** Author for correspondence

***Serbian Chemical Society active member

found in the top 30 cm layer is 0.05–0.1 Bq/kg. The purpose of the present research was, therefore, to investigate the possibility of preconcentration of Am-241 from a large mass of sample, followed by high sensitivity gamma counting in a low energy gamma detector.

EXPERIMENTAL

Reagents and apparatus

All chemicals were of analytical reagent grade. The measurements were performed with a Canberra low energy (LEGe) detector using a cylindrical plastic container, 60 mm in diameter and 48 mm total height. The spectra were accumulated with a Canberra multichannel analyzer. The characteristics of the applied detector are given in Table I. The detector was calibrated using a mixed radionuclide standard.

TABLE I. Characteristics of the detector used in gamma spectrometry of Am-241

| Geometry | Coaxial open end, closed and facing window |
|----------------------|--|
| Diameter | 53.5 mm |
| Length | 53.0 mm |
| Distance from window | 5 mm |

The measurements of activity by gamma spectroscopy depend on numerous factors, including the geometry of the sample and its self-absorption. A sample of 16 mm height was used as the reference and any sample with a different height was normalized to the reference height by using Eq. (1) which was determined by geometry experiments

$$f = \frac{0.97239 + 0.02314 h}{1.342672} \quad (1)$$

where h is the height of the sample in mm.

Alpha spectrometry was performed using Canberra PIPS detector; eight inputs counting into a Series 35 MCA; energy range 3.5–7.0 MeV.

Sample preparation

Sediment cores were collected during 1998 from different sites of the lagoon of Venice and stored at 4 °C until sectioned. The cores, about 80 cm long, were cut into 15 cm long sections.

For the work with a tracer, marine sediments (60–80 cm layers), where no ²⁴¹Am was initially present, were used. Into approximately 700 g of wet sample was added 0.1 ml of Am-241 tracer solution. Then the sample preparation included drying at 105 °C, removal of pebbles and shell fragments, grinding to less than 200 mesh and burning at 180 °C. Finally, the sample was ignited in a metal crucible in a muffle oven at 600 °C to destroy any organic matter. The resulting ash was analyzed by gamma spectroscopy and these samples with known Am-241 activity (10–15 Bq/kg of ignited sample) were used for the examination of the leaching procedure efficiency. Ash samples were leached for 30 min with appropriate amount of boiling conc. HNO₃ (50 cm³ per 50 g at 600 °C ignited sediment). After cooling, the solution was centrifuged and the residue was treated three times with 7.5 M HNO₃. All the liquid fractions were combined and the americium was coprecipitated with calcium as a partial oxalate precipitate from the total volume of the leaching solution. The obtained CaC₂O₄ precipitate was measured by gamma spectroscopy.

The examined sections of a few cores were mixed together and carefully homogenized. The samples were ignited using previously described procedure for the samples with tracer and 50 g of each sample was separated for the determination of Am-241 by alpha spectroscopy with Am-243 as a tracer.⁵

The appropriate amount of the examined samples was leached using the same procedure as described for the samples with tracer. The solution was made up to 1 dm³ with distilled water, warmed at 80 °C and 200 g of H₂C₂O₄·2H₂O was added with constant stirring. The pH was adjusted to 0.5 with ammonia. The comparatively large amount of oxalic acid is necessary because iron reacts with oxalic acid to form a soluble complex.⁶ After settling, the precipitate was separated by filtration (membrane filter, 1.2 µm pore size) while still hot, rinsed several times with washing solution⁷ to remove traces of iron and dried for 30 min at 105 °C. Then the calcium oxalate precipitate was ignited at 550 °C and measured by gamma spectroscopy. If the amount of the resulting carbonates was large, they were dissolved in conc. HCl and the americium was recovered from the solution by a second precipitation of calcium oxalate by adding a significantly smaller amount of oxalic acid (approx. 10 g). The precipitate was collected on a membrane filter (Millipore 1.2 µm), rinsed several times with washing solution and measured by gamma spectroscopy. Also, if the precipitate was yellow due to a high content of Fe, repeated coprecipitation was required to achieve an adequate decontamination. The addition of a second precipitation resulted in minimal increase in processing time but provided better separation and a chemically pure fraction.

Even when 200 g of oxalic acid was added to the solution at pH 1.5, precipitation of Fe(OH)₃, due to high content of iron in the sample, was observed. These samples were then treated using the previously described procedure for large samples of calcium oxalate to remove the iron present.

Precipitation of Fe(OH)₃ and Am(OH)₃ from some samples was also performed by changing the pH by adding NaOH since the pH of the leaching solution was very low and it was necessary to add a significant amount of sodium hydroxide to increase the pH to 8. Also, from these samples, after dilution of the obtained hydroxides in HCl, calcium oxalate was precipitated by adding 100 g of oxalic acid to complex the iron and to precipitate Ca ions previously coprecipitated on Fe(OH)₃. The amount of the CaC₂O₄ obtained was very low and this precipitate was measured by gamma spectroscopy immediately after filtration.

RESULTS AND DISCUSSION

Due to at the moment extremely low-activity concentration of ²⁴¹Am from global fallout, a large amount of the material has to be leached to obtain reasonably small errors for the activity concentration. In the series of experiments with tracer the leaching process was optimized because it was necessary to separate Am from 300 g or more of burned sample in order to reach the limit of detection of the instrument. As shown in Fig. 1, although good recoveries using calcium oxalate were obtained for 100 g soil samples, with 200 g the recovery fell to around 85 % and with 930 g to 73%. Obviously the leaching procedure is a very important stage and so separate portions of 100 g at 600 °C ignited sediments were leached for all experiments without tracer.

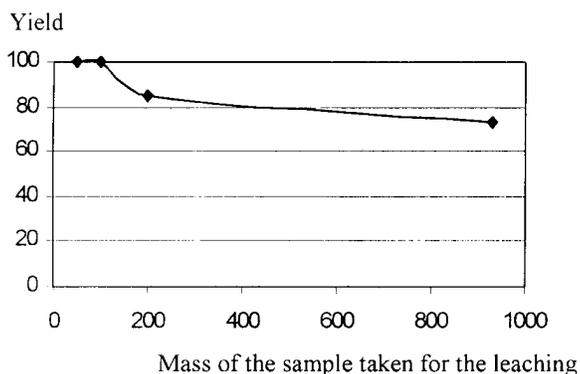


Fig. 1. The influence of the mass of sediment taken for leaching on the yield of americium-241.

Sample 1 was prepared by mixing section B (15–30 cm) of six cores. Samples 2 and 3 were prepared by mixing section C (30–45 cm) of 6 and 12 cores, respectively. The three different procedures described above were applied for the treatment of 1 kg of each sample prior to gamma spectroscopy. The series of experiments are summarized in Table II. For large soil samples, the removal of Am was quantitative, but the loading of iron resulted in long counting times and sometimes two precipitations of CaC_2O_4 were included in order to obtain low mass and white precipitates. The agreement between the well known alpha method and the low energy gamma spectroscopy was within 8 % in spite of the differences in of procedures used.

TABLE II. Yield of Am-241, the influence of coprecipitation

| Sample | Precipitate | Mass of CaC_2O_4 precipitate/g | Am-241/(Bq/kg) |
|---------------|--|--|----------------|
| 1 (section B) | $\text{Fe}(\text{OH})_3$, pH 8.0 then Ca oxalate | 7.5 | 0.145 |
| 2 (section C) | $\text{CaC}_2\text{O}_4 + \text{Fe}(\text{OH})_3$, pH 1.5 then Ca oxalate | 21.44 | 0.06 |
| 3 (section C) | CaC_2O_4 , pH 0.5 | 30.6 | 0.072 |

In order to verify the overall procedures, seven different samples were prepared for the determination of Am-241 by mixing appropriate amounts of sections A and B. Also the influence of dilution was examined since Am is present in the first layer (0–15 cm) in very low activity concentrations under undisturbed conditions.

TABLE III. Experimental conditions (C-Chioggia, V-Venice)

| Sample | Mass of the wet sample taken for combustion. Section A + section B/g | Mass of the sample after combustion at 600 °C/g | Mass of the sample taken for leaching/g |
|--------|--|---|---|
| 13 C | 750 + 750 | 420.64 | 370.6 |
| 17 C | 700 + 700 | 485.8 | 485.8 |
| 48 C | 800 + 800 | 536.23 | 486.1 |
| 60 C | 1000 + 1000 | 488.7 | 436.1 |
| 18 V | 750 + 685 | 661.1 | 611.1 |
| 28 V | 750 + 750 | 600.28 | 550.28 |
| 9 Vx | 1000 + 1000 | 911 | 856.2 |

The data of each matrix analyzed are summarized in Table III. The results obtained with these seven cores are given in Table IV. Also the heights of the samples measured by gamma spectroscopy are given since the height has an influence on the measurements. The comparatively low recovery of samples 13 C and 60 C is only due to counting errors because the activity concentration of the starting sample was very low.

TABLE IV. Results for Am-241 by gamma counting

| Sample | Height of the sample/mm | Am-241/(Bq/kg) | Yield/(%) |
|--------|-------------------------|----------------|-----------|
| 13 C | 14 | 0.045 | 85 |
| 17 C | 18 | 0.063 | 100 |
| 48 C | 5 | 0.068 | 100 |
| 60 C | 20 | 0.021 | 80 |
| 18 V | 7 | 0.054 | 100 |
| 28 V | 16 | 0.075 | 100 |
| 9 Vx | 7 | 0.046 | 90 |

The obtained results indicate that the applied method can often replace the more time consuming and elaborate radiochemical technique traditionally used in measuring low-level activity of Am-241 in natural samples. Furthermore, the need for using expensive high-purity Am-243 tracer and electrodeposition equipment and procedures is also completely eliminated. This concentration technique has the advantage of processing large samples and it permits substantial improvements in the determinations.

ИЗВОД

ОДРЕЂИВАЊЕ АМЕРИЦИЈУМА-241 ГАМА СПЕКТРОСКОПИЈОМ

МИРЈАНА Ђ. РИСТИЋ^{1*}, САНДРО ДЕГЕТО² и ТЕОДОР АСТ¹

¹Технолошко-металуршки факултет, Карнегијева 4, Београд, Југославија и ²Istituto di Chimica e Tecnologia del CNR, Corso Stati Uniti 4, I 35020 Padova, Italy

Испитана је могућност преконцентрисања Am-241 из велике масе седимента (1–2 кг) пре његовог одређивања гама спектроскопијом. Сепарација је вршена да би се сав Am-241 издвојио на погодном носачу, односно да би се достигла граница осетљивости инструмента, јер је Am присутан у седиментима у изузетно малим количинама (0,01–0,5 Bq/kg). Серијом експеримената са обележивачем одређен је степен сепарације добијен копреципитацијом. Примена методе на узорке седимената са различитим садржајем америцијума показала је да је слагање резултата добијених овом методом са резултатима добијеним алфа спектроскопијом било 10 %.

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REFERENCES

1. A. R. Byrne, A. Komosa, *The Science of Total Environment* **130/131** (1993) 197
2. D. S. Sill, C. W. Sill, *Radioactivity and Radiochemistry*, Vol. 5, No.2 (1994) 8
3. E. P. Horwitz, M. L. Dietz, D. M. Nelson, J. J. La Rosa, W. D. Fairman, *Anal. Chim. Acta* **238** (1990) 263
4. S. J. Goldstein, C. A. Hensley, C. E. Armenta, R. J. Peters, *Anal. Chem.* **69** (1997) 809

5. K. Bunzl, H. Förster, W. Kracke and W. Schimmack, *J. Environ. Radioactivity* **21-22** (1993) 11
6. K. Bunzl, W. Kracke, *Radioanalytical and Nucl. Chem.* **138** (1990) 83
7. A. I. Vogel, *Quantitative Inorganic Chemistry*, Longmans, 1961, p. 541.