

RiO5 METHOD (31)

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Cs, Sr, Ru, Ce, Pm — alpha, beta, gamma — water

Determination of fission-products and actinides in water

Disclaimer

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1 SCOPE

The following analytical scheme has been used for low level radionuclide analysis on 10 to 20 liters of seawater. It permits the separation and measurement of ^{134}Cs , ^{137}Cs , ^{90}Sr , ^{106}Ru , ^{239}Pu , ^{240}Pu , ^{147}Pm , and ^{144}Ce . The entire procedure is outlined in the flow chart in the flow diagram.

2 PROCEDURE

- The sample is first acidified with 3M HCl to pH 1.5 in original storage container (10 or 20 liter plastic cubitainer).
- Carriers and a-acers are added (10 mg Cs, 2 g Sr, 20 mg Ru, 0.1 mg Nd, 10 mg Ce, 2 mg Fe, and 0.05 mBq ^{242}Pu for mass spectrometric Pu analysis), and the sample is heated at 60°C for at least 48 hours to allow for tracer equilibration.
- The hydroxides (containing Ru, Nd, CE, Pm, and Pu) are precipitated at pH 9 with 10M NaOH. We have found that it is important to use NaOH rather than NH_4OH to optimize Cs recovery when co-precipitating Cs with ammonium molybdophosphate (AMP) in subsequent steps.
- The hydroxides are allowed to settle and the supernate, containing Cs and Sr, is decanted.
- Cesium is then concentrated with AMP, purified, and mounted for counting as a Cs-chloroplatinate precipitate; Sr is precipitated as an oxalate and processed according to published procedures.
- The hydroxides are dissolved with 6M HCl, diluted with deionized water (DI H₂O), and reprecipitated with NH_4OH , centrifuged and dissolved in 25 ml of 9M H₂SO₄.
- This is transferred to a distillation flask for the separation of Ru from Pu and the rare earth elements.

A. Ruthenium Analysis

- The distillation flask used has an air inlet as well as a vapor outlet which extends into a 60-ml centrifuge tube containing 30 ml of 6M NaOH placed in an ice bath. One gram of KMnO_4 is added to the sample in the flask to oxidize the Ru to RuO_4 .
- Air is gently bubbled through the sample while heating to 90°C for 30 minutes. Under these conditions, the RuO_4 is distilled into the NaOH solution.
- The distillate is allowed to cool, another gram of KMnO_4 is added, and the distillation process is repeated to assure complete distillation of Ru.

- The RuO₄ is reduced to ruthenium dioxide (RuO₂) by the addition of 1ml of ethanol to the distillate and heating in a boiling water bath until black RuO₂ forms.
- The sample is centrifuged and the supernate, if clear and colorless, is discarded. If a blue-green supernate is present, indicating incomplete precipitation of the RuO₂, the solution must be neutralized with HCl and 1 ml 6M NaOH is added.
- • The heating with ethanol is repeated and the sample is centrifuged. The RuO₂ precipitate is dissolved in 2 ml of concentrated HCl and diluted to 20 ml with DI H₂O.
- Powdered magnesium metal is added in small increments to the dissolved RuO₂ to reduce it to black Ru metal. This is done in a hot water bath until the Ru metal precipitates and the solution becomes clear and colorless.
- Concentrated HCl is added dropwise to dissolve any excess Mg metal.
- The sample is cooled and centrifuged.
- The Ru is washed with boiling DI H₂O and filtered onto a tared 25 mm diameter Millipore type HA 0.45 μm filter, rinsed with DI H₂O followed by ethanol.
- After drying at 60°C, the sample is weighed and a yield is computed. (Typical chemical recoveries for Ru ranged from 50-70%. The precipitate of metallic Ru contains a small amount of oxide, therefore standardization of the Ru carrier is made under the same conditions).
- The Ru carrier solution contains ruthenium (111) chloride trihydrate, RuCl₃•3H₂O, dissolved in 0.1M HCl and diluted to yield a 20 mg Ru/g solution.
- Six weighed aliquots of the carrier, containing 2.25 mg Ru, are transferred to Erlenmeyer flasks, diluted with 25 ml DI H₂O, and acidified with 2 ml 12M HCl.
- Powdered Mg (0.4 g) is added in small increments, shaking after each addition.
- The samples are boiled gently until the Ru coagulates and the supernates are clear and colorless. An additional 10 ml of 12M HCl is added slowly to dissolve any excess Mg.
- The samples are boiled gently for two minutes, allowed to cool, and filtered onto tared 25 mm diameter Millipore type HA 0.45μm filters; each being washed three times with 5 ml of hot DI H₂O, followed by ethanol.
- The filters are dried at 60°C for 30 minutes and weighed.
- The Ru filters are mounted for counting on a lucite card and covered with a film of Mylar (0.9 mg/cm²).
- A 45 mg/cm² foil is placed over the samples to effectively absorb any 0.3 MeV or under beta emitting interference.
- The determination of ¹⁰⁶Ru activity in the sample is made by low-level beta counting of the 3.5 MeV ¹⁰⁶Ph daughter.

- Six standards were prepared to establish the detector counting

B. Plutonium Analysis

- After the Ru separation, the distillate containing residues of KMnO_4 is dissolved in 3M HCl and the solution is cleared with 30% H_2O_2 .
- The hydroxides, containing Pu and the rare earth elements, are precipitated at pH 9 with concentrated NH_4OH .
- The precipitate is dissolved in 100 ml of 8M HNO_3 .
- Plutonium is oxidized to the quadrivalent state with 1.0g NaNO_2 and adsorbed onto an anion exchange resin column (25 ml volume containing BioRad AG I X 8 resin, 50-100 mesh).
- The rare earth elements pass through the column in the initial HNO_3 solution and subsequent 300 ml 8M HNO_3 wash (a minor amount, ~10% of Ce remains on the column) and are held for further purification.
- The column is washed with 150 ml of 12M HCl, and Pu is eluted from the column with 100 ml of 12M HCl containing 5 ml of 1M NH_4I .
- The eluate is dried and held for further purification prior to analysis of ^{239}Pu and ^{240}Pu by mass spectrometry.

C. Rare Earth Elements Analyses

The purification of the rare earth element fraction is based upon the separation of ^{147}Pm from ^{144}Ce by ion exchange and the use of stable Nd and Ce as yield monitors for ^{147}Pm and ^{144}Ce , respectively. The procedures are adapted from Shirey et al.

- The rare earth element eluate from the Pu column is evaporated to 25 ml and diluted to 400 ml with DI H_2O . The stable Ce carrier permits the co-precipitation of rare earth oxalates in an excess of oxalic acid.
- The oxalate precipitate (containing Ce, Nd, and Pm) is dissolved in 16M HNO_3 , evaporated to dryness and resolubilized in a minimum volume (0.5-1.0 ml) of 0.2M 2-methylsuccinic acid (2-hydroxy-isobutyric acid) at pH 4.6.
- The solution is loaded onto a column (2 mm I.D., 35 cm length) containing 1 ml of BioRad AG 50W x 4, <400 mesh resin.
- A positive pressure of 0.4 atmospheres is applied to the column via tank nitrogen. • An optical sensor (Model 9100, Accura Flow Products Co.) is attached to a counter (CUB-2000, Empire Electric Co.) to monitor the number of drops eluted from the column (approximately one drop per minute; 1 drop = 0.05 ml).

- After the sample solution has been loaded onto the resin, approximately 10 ml of 0.2M 2-methylactic acid (pH 4.6) is added to the reservoir above the resin.
- The first 2 ml eluted are discarded as they contain the heavy rare earth elements.
- Promethium is eluted from the column in the next 4.25 ml fraction (drops 40-125).
- Iron carrier (1 mg Fe as FeCl₃) is added to the Pm fraction and Pm is quantitatively co-precipitated with Fe(OH)₃ at pH 9 with 14M NH₄OH.
- The precipitate is carefully collected onto a 25 mm Millipore type HA 0.45 μm filter and dried at 60°C.
- The filter is mounted on a lucite card, covered with Mylar film (0.9 mg/cm²), and ¹⁴⁷Pm (225 keV) is counted via low-level beta detection.
- Three standards are prepared to establish the detector counting efficiency for the ¹⁴⁷Pm samples. Each standard contained 10 Bq ¹⁴⁷Pm (Amersham ¹⁴⁷Pm standardized solution) in 2 ml of 0.2M 2-methylactic acid at pH 4.6.
- The standards for detection efficiency were precipitated, mounted and counted in a manner similar to the samples.

The Nd eluate is collected in the next 2.5 ml fraction (drops 126-175) for the determination of the chemical yield of ¹⁴⁷Pm.

- An aliquot of approximately 10% (by weight) of the Nd eluate is used in the yield titration. Eriochrome Black T (0.25 ml) is added as a pH-sensitive colorimetric indicator of the presence of the rare earth elements (pink).
- The pH of the aliquot is adjusted to 7.0 with 0.1M triethenolamine (TEA). The amount of Nd present in the aliquot is determined colorimetrically by titration from pink: to a blue endpoint with 10⁻⁴M EDTA. The Nd carrier solution contains pure neodymium oxide, Nd₂O₃ (from Alfa Division Ventron), dissolved in 1M HNO₃, and diluted to yield a calibrated 100 μg Nd/g solution. (Typical chemical recoveries for ¹⁴⁷Pm ranged from 30-75%.)
- The eluting acid is changed to 2.5M HNO₃ and the first 0.5 ml of the eluate is discarded.
- Cerium is eluted in the next 4.5 ml (90 drops).
- An aliquot of approximately 5% (by weight) of the Ce eluate is used for the determination of the chemical yield of ¹⁴⁴Ce.
- Eriochrome Black T (0.25 ml) is added, the pH is adjusted to 7.0 with 1M TEA. and the solution is titrated to a blue endpoint with 10⁻³M EDTA, in a manner similar to the Nd determination. (Typical chemical recoveries for ¹⁴⁴Ce ranged from 30-70%.)
- Iron carrier (1 mg Fe) is added to the Ce fraction to be counted, and the Ce is quantitatively co-precipitated with Fe(OH)₃, filtered and mounted identically to ¹⁴⁷Pm.

- The combined ^{144}Ce (320 keV) and ^{144}Pr (3.0 MeV) daughter signals are counted via low-level beta detection.
- The Ce carrier solution contains Ce(III) chloride heptahydrate, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, dissolved in 0.01 M HNO_3 and diluted to yield 10 mg Ce/g solution. In order to standardize the Ce carrier, three weighed aliquots of the carrier were transferred to 2-liter beakers, diluted to 500 ml with DI H_2O and 1hc oxalates precipitated at pH 1.0 with saturated oxalic acid.
- The cerium oxalates were filtered through tared 7-cm diameter Whatman #42 filter papers, washed with DI H_2O , and dried in a vacuum desiccator for five minutes.
- The cerium oxalates were placed in tared ceramic crucibles and heated at 800°C for 30 minutes.
- The resulting cerium dioxide, CeO_2 , was weighed to establish the concentration of Ce in the carrier solution.
- Eight counting standards were prepared to establish the detector counting efficiency for ^{144}Ce .
- The eight standards consisted of two replicates containing 0, 3, 7 or 10 mg of stable Ce, in addition to
- 2.8 Bq of ^{144}Ce (Amersham ^{144}Ce standardized solution) in a 2.5M HNO_3 matrix.
- The counting standards were precipitated, mounted and counted as the samples had been.

LARGE VOLUME CHEMISORPTION SAMPLES

Seawater is pumped (Flotec flexible impeller pump) at 5-8 liters/minute from 0.5 m beneath the surface water, through five in-line cartridges which serve as radionuclide collectors. The first cartridge serves as a pre-filter and consists of a wound $0.5 \mu\text{m}$ nominal pore-sized polypropylene filter (CUNO Microwynd DPPPZ) which collects the particulate radionuclides. Following this pre-filter are two MnO_2 -coated wound cotton cartridges which are used to extract dissolved actinides.

The collection efficiency for the dissolved radionuclides is determined by the difference in activity between the rust first and second MnO_2 cartridge. Following the MnO_2 cartridges are two cupric ferrocyanide-based $(\text{CuFe}(\text{CN})_6)$ Cs adsorber cartridges. (Dissolved Cs, which passes through the first three cartridges, is efficiently collected on these cartridges). The Cs collection efficiency is determined in the same way as for the MnO_2 cartridge pair.

- The pre-filter is placed in a 2-liter beaker with a foil cover and ashed at 400°C for 24
- The ash is transferred to a 6.5 cm diameter plastic jar and counted directly on a Ge(Li) detector for particulate ^{106}Ru , ^{144}Ce , ^{137}Cs , and ^{134}Cs .

- For particulate Pu, Am, and Cm isotopes, the ashed filters are digested in hot 8M HNO₃ in the presence of chemical yield monitors (10 mBq of ²⁴²Pu and 20 mBq of ²⁴³Am), followed by radiochemical purification, electrodeposition, and alpha counting.

3 REFERENCES

Buesseler, K.O., Casso, S.A., Hartman, M.C., Livingston, H.D. (1990) Determination of fission-products and actinides in the Black Sea following the Chernobyl accident. *Journal of Radioanalytical and Nuclear Chemistry*, 138:1, 33-47.

4 FLOW CHART

