

TENTATIVE METHOD FOR THE DETERMINATION OF
PLUTONIUM-239 AND PLUTONIUM-238 IN WATER
(BY A COPRECIPITATION ANION EXCHANGE TECHNIQUE)

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PREFACE

The analytical procedure described in this document is a method for the determination of plutonium in water which is being collaboratively tested according to an interagency agreement between the U.S. Environmental Protection Agency (USEPA) and the U.S. Energy Research and Development Administration (USERDA). Data from the collaborative test will be examined and information on the precision and accuracy of the method will be obtained. Final USEPA and USERDA documents will be prepared describing the results of the collaborative test.

In order to obtain a method for collaborative testing, the scientific literature on the determination of plutonium in water was first examined. Based on certain established criteria, a method from the literature was chosen and tested. Similar methods were tested and modifications were made until a final procedure was established. One of the principle criteria was that the method be cost effective. Thus the method that was finally adopted uses techniques that are relatively simple, and it is also designed to handle a large number of samples. Also the equipment and reagents are generally common to the analytical laboratory.

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WATER ANALYSIS PROCEDURE

1. Scope and Application

- 1.1 This procedure has been successfully tested and is applicable to both fresh water and sea water samples. It can be applied to sample volumes of a liter to 20 liters or more. In laboratories where the background of the counters is less than a count per 1000 minutes in the Pu-239, Pu-240, or the Pu-238 regions, and where reagent blanks contribute less than counter background, as little as a few femto-curies of plutonium can be determined when the sample is counted for a few days.

This method applies to soluble plutonium and to suspended particulate matter containing plutonium. When the latter situation occurs, an acid dissolution step is added to the procedure to assure that all of the plutonium dissolves.

- 1.2 The minimum detectable concentration of plutonium in water depends on the volume of water analyzed. The minimum detectable activity (MDA), that amount of activity which in the same counting time, gives a count which is different from the background count by three times the standard deviation of the background count, can be estimated from some typical parameters that might be expected from the present procedure.

Consider a sample that is counted for 1000 minutes on an alpha spectrometer having a 25% counting efficiency and a five count per 1000 minute background in the energy region of interest, and shows a 60% chemical recovery. Based on the definition of the MDA, the sample count would have to be 7 ($\sqrt{3} \times \sqrt{5}$), and to achieve this count under the conditions stated would require 0.045 d/m of activity. Thus, a typical MDA for plutonium in water by this procedure would be 0.05 d/m.

- 1.3 The precision of the method has not yet been extensively evaluated, but it is expected to approach that of the counting statistics errors. The accuracy is expected to be within limits propagated from counting statistics and the uncertainty in the specific activity of the tracer used.

1.4 This method was selected since it can be readily used by a laboratory technician. It does not involve any particularly sophisticated steps and after training by a chemist who understands the chemistry and the counting involved, the procedure can be routinely carried out by a technician.

2. Summary

The procedure consists of a coprecipitation, an anion exchange separation and electrodeposition, followed by alpha pulse height analysis. More specifically, the sample is acidified with nitric acid and plutonium-242 is added as a tracer before any chemical separations are performed. Iron is added to the water as iron (III) and the plutonium is coprecipitated with the iron as ferric hydroxide by adding ammonium hydroxide. After decantation and centrifugation, the ferric hydroxide precipitate containing the coprecipitated plutonium is dissolved and the solution is adjusted to 8M in HNO₃ for anion exchange separation. When the sample fails to dissolve because of the presence of insoluble residue, the residue is treated by a rigorous acid dissolution using concentrated nitric acid and hydrofluoric acids.

The sample is poured over an anion exchange column. The iron and most other elements that might be present pass through the column. Thorium is removed from the column with 12 M hydrochloric acid and then the plutonium is eluted by reducing it to plutonium (III) with the iodide ion. The plutonium is electrodeposited onto a stainless steel slide for counting by alpha pulse height analysis using a silicon surface barrier detector. From the recovery of the plutonium-242 tracer, the absolute amounts of plutonium-238 and plutonium-239 can be calculated, and from the volume of sample analyzed the concentrations of these two isotopes in the water sample can be calculated.

3. Interferences

3.1 The procedure is such that no other alpha emitting radioisotopes should appear along with the plutonium in the final counting step. The procedure has been tested with uranium, americium, thorium and polonium isotopes to verify the fact that these elements are separated out by anion exchange, and thus do not electrodeposit with the plutonium.

- 3.2 In determining low levels of plutonium in environmental samples, it is essential to make blank determinations to ascertain that the contamination from reagents, glassware and other laboratory apparatus is negligible. A blank value should be determined in exactly the same way as a sample value.

4. Apparatus

4.1 Instrumentation

- 4.1.1 Alpha Pulse Height Analysis System - The system uses an ORTEC silicon surface barrier detector and is capable of giving a resolution of 50 keV or better with samples electrodeposited on flat mirror finished stainless steel slides. The resolution here is defined as the width of the alpha peak in keV, when the counts on either side of the peak are equal to one-half of the counts at the maximum of the peak. The counting efficiency of the system should be greater than 15% and the background in the energy region of each peak should be less than 10 counts in 1000 minutes.
- 4.1.2 Electrodeposition Apparatus - A constant current power supply, 0-12 V, 0-2 A, is required for the electrodeposition described in this procedure. A disposable electrodeposition cell is also required. An apparatus similar to that shown in Figure 1 has been used in the present procedure. In the present procedure, the cell itself is surrounded by water, but the water is not circulated. The electrodeposition can be carried out without the water cooling.

The cathode is a stainless steel slide pre-polished to a mirror finish. The diameter of the slide is 3/4" and the exposed cathode area during electrodeposition is 2 cm².

The anode is a 1 mm diameter platinum wire with an 8 mm diameter loop at the end, above the cathode disk.

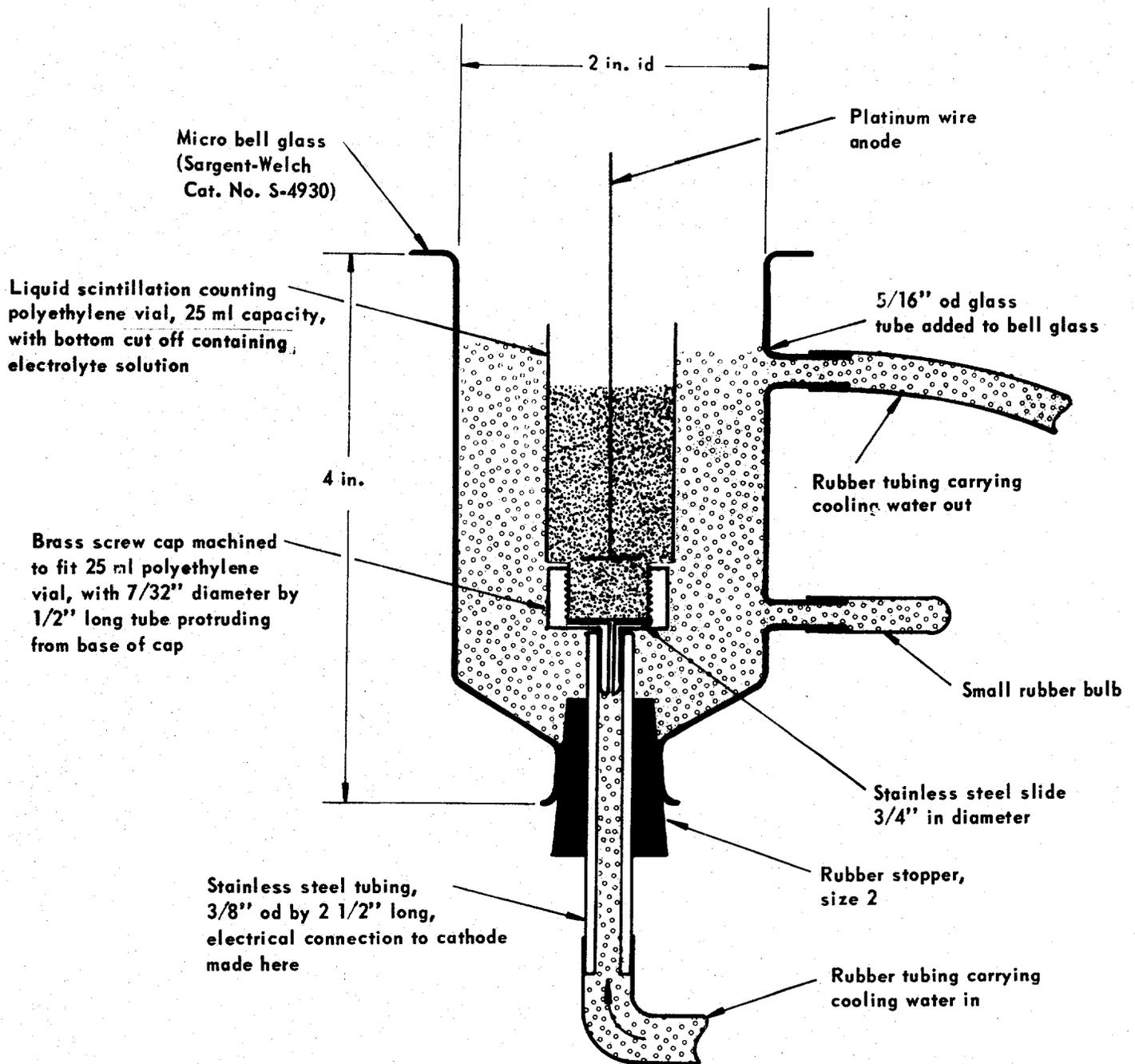


Figure 1. Water Cooled Electrodeposition Apparatus

4.2 Laboratory Equipment

- 4.2.1 Balance - top loading, capacity 1200 g, precision ± 0.1 g
- 4.2.2 Hot plate - magnetic stirrer and stirrer bar
- 4.2.3 Peristaltic pump with pumping capacity of 4 liters per minute (required only for samples of several liters or greater)
- 4.2.4 Centrifuge - capable of handling 100 ml or larger centrifuge bottles (a larger centrifuge is required for handling 10 liter or larger samples)

4.3 Labware

- 4.3.1 Graduated cylinders - 5 ml to 1000 ml
- 4.3.2 Beakers - glass, 100 ml to 2 liters
- 4.3.3 pH paper - pH range 2 to 10
- 4.3.4 Automatic pipets - with disposable tips, volumes between 100 μ l and 1000 μ l
- 4.3.5 Centrifuge bottles - 100 ml or greater (larger bottles are required for 10 liter or larger samples)
- 4.3.6 Ion exchange columns - approximately 1.3 cm ID, 15 cm long with 100 ml reservoir
- 4.3.7 Pipets - glass, class A
- 4.3.8 Disposable pipets - 2 ml glass eye-dropper type, with rubber bulb
- 4.3.9 Dropping bottles
- 4.3.10 Watch glasses
- 4.3.11 Polyethylene washing bottles
- 4.3.12 Glass stirring rods

4.4.13 Beaker tongs

4.3.14 Spatulas

4.3.15 Heat lamp - mounted on ring stand for drying slides

5. Standards, Acids, Reagents

5.1 Standards

5.1.1 National Bureau of Standards (NBS) plutonium-242 solution (SRM #4334 or #4335) with the concentration certified to $\pm 1\%$ of its stated activity, or a dilution of this standard

5.2 Acids - reagent grade, meeting American Chemical Society (ACS) specifications; diluted solutions prepared from distilled deionized water.

5.2.1 Nitric acid - concentrated (16 M), 8 M

5.2.2 Hydrochloric acid - concentrated (12 M), 0.5 M

5.2.3 Sulfuric acid - concentrated (18 M), 1.8 M

5.2.4 Hydrofluoric acid - concentrated (48% solution)

5.2.5 Boric acid - powder or crystalline

5.3 Reagents - reagent grade, meeting ACS specifications, solutions prepared from distilled deionized water

5.3.1 Ferric chloride - in 0.5 M HCl to give 50 mg of iron per ml of solution

5.3.2 Ammonium hydroxide - concentrated (15 M), 1.5 M, 0.15 M

5.3.3 Sodium nitrite

5.3.4 Anion exchange resin - Bio Rad AG1-X8 (100-200 mesh) chloride or nitrate form. (Available from Bio Rad Laboratories, 3rd and Griffin Ave., Richmond, Calif., 94804). A column is prepared by slurring this resin with 8 M HNO₃ and pouring it onto a column of inside diameter approximately 1.3 cm. The height of the column of resin should be about 8 cm, or greater for samples containing suspended matter or for larger volume samples. The resin is then converted to the nitrate form by passing 10 column volumes of 8 M HNO₃ through the column.

- 5.3.5 Ammonium iodide - 1 M.
- 5.3.6 Sodium hydrogen sulfate - ~5% in 9 M H₂SO₄; dissolve 10 g of the NaHSO₄ in 100 ml of water and then carefully add 100 ml of 18 M H₂SO₄.
- 5.3.7 Preadjusted electrolyte - 1 M ammonium sulfate adjusted to pH 3.5 with 15 M NH₄OH and 18 M H₂SO₄.
- 5.3.8 Thymol blue indicator, sodium salt (available from Fisher Scientific Company) - 0.04% solution.
- 5.3.9 Ammonium nitrate - 1% in 0.15 M NH₄OH.
- 5.3.10 Ethyl alcohol - made slightly basic with a few drops of 15 M NH₄OH per 100 ml of alcohol.

6. Calibration and Standardization

- 6.1 Standardization of the Plutonium-242 Tracer Solution
This tracer is available from the National Bureau of Standards (NBS) as SRM #4334 or #4335. The overall uncertainty of the concentration of the plutonium-242 is +1.0%.

If a laboratory desires to standardize its own solution, aliquots of the solution could be mounted on slides and counted with a 2 π proportional counter. The efficiency of the 2 π counter must accurately be determined with an NBS alpha point source, making corrections for resolving time and backscattering if necessary.

- 6.2 Determination of Alpha Spectrometer Efficiency

An accurate determination of the alpha spectrometer counting efficiency is not necessary to get an accurate concentration of plutonium isotopes in the sample being analyzed. This is because of the fact that when a tracer is used, the counting efficiency is the same for the tracer and the unknown plutonium isotopes, and is not needed to calculate the unknown plutonium concentrations (cf. section 8.1).

An approximate determination of the alpha spectrometer counting efficiency is required to calculate the plutonium recovery of a particular analysis. To determine this efficiency, requires that one count an alpha particle source of a known alpha particle emission rate under the same conditions that the samples are counted. The alpha particle counting efficiency is then calculated as illustrated in section 8.2.

7. Step By Step Procedure For Analysis

7.1 Coprecipitation

- 7.1.1 Weigh or measure the volume of a one liter or larger water sample.
- 7.1.2 If the sample has not been acidified, add 5 ml of 16 M HNO₃ per liter of sample.
- 7.1.3 Mix the samples completely using a magnetic stirrer for small samples, or a peristaltic or other pump for larger samples. Check the acidity with pH paper. If it is greater than 2, add 16 M HNO₃ until it reaches this value.
- 7.1.4 Add standardized Pu-242 tracer with a calibrated pipet (or add a weighed amount of the tracer) to give about 10 dis/min of Pu-242. If the Pu-238 or Pu-239 content of the sample is known to be high, use Pu-236 tracer.
- 7.1.5. Mix the sample for about one hour or longer if the sample volume is greater than a few liters. (If the sample volume is only a few liters, it is advisable to heat the water to 50-60°C while stirring.)
- 7.1.6 Add 50 mg of iron as FeCl₃ in 0.5M HCl to a one liter sample (or more iron, up to 1 gram, to a sample of a few hundred liters).
- 7.1.7 Stir again for ten minutes or longer if the sample volume is greater than a few liters. (If

the sample volume is only a few liters or less, heat the sample to boiling).

- 7.1.8 Add 15 M NH_4OH while stirring to precipitate the iron. Add a slight excess of 15 M NH_4OH to raise the pH to 9-10 as determined with pH paper.
- 7.1.9 Continue to stir the sample for 30 minutes, or longer for samples with a volume greater than a few liters, before allowing it to settle.
- 7.1.10 After the sample has settled sufficiently, decant the supernate, being careful not to remove any precipitate. (If the analyst wishes to continue immediately, the iron hydroxide may be filtered out at this time).
- 7.1.11 Slurry the remaining precipitate and supernate and transfer to a centrifuge bottle. If larger samples of water are being analyzed, it is necessary to transfer the slurry to a large beaker and allow it to settle again.
- 7.1.12 Centrifuge the sample and pour off the remaining supernate.
- 7.1.13 Dissolve the ferric hydroxide with a minimum of 16M HNO_3 . (If organic matter is present, it may be necessary to treat the sample with 30% H_2O_2 and 16 M HNO_3 to remove it.)
- 7.1.14 If the precipitate dissolves completely, add a volume of 16 M HNO_3 equal to the volume of the sample solution, dilute to 100-150 ml with 8 M HNO_3 , and then proceed to Section 7.3, Anion Exchange Separation. If the precipitate does not dissolve in nitric acid, proceed to section 7.2 Acid Dissolution of Insoluble Residue.

7.2 Acid Dissolution of Insoluble Residue

- 7.2.1 When the precipitate fails to dissolve in nitric acid, add more 16 M HNO_3 to a total volume of about 75 ml, transfer the entire sample to a teflon beaker, and add 75 ml of 48% HF. (CAUTION: HF is extremely hazardous. Wear rubber gloves, safety glasses or goggles and a lab coat. Clean up all spills and wash thoroughly after using HF. Avoid breathing any HF fumes.)
- 7.2.2 Add a teflon coated stirring bar and heat on a magnetic stirrer hot plate for about 4 hours at a temperature near boiling. Add equal amounts of 16 M HNO_3 and 48% HF to keep the volume at about 150 ml.
- 7.2.3 Allow the mixture to cool, and decant the solution into another teflon beaker.
- 7.2.4 Evaporate this solution to dryness.
- 7.2.5 While this solution is drying, add 75 ml of 12 M HCl and 2 g of H_3BO_3 to the undissolved residue. Stir and let stand until the solution from the previous step has evaporated to dryness.
- 7.2.6 Transfer the HCl- H_3BO_3 mixture from the last step to the dried sample, leaving any residue behind. Rinse the residue once with water and transfer the water to the sample.
- 7.2.7 Evaporate the sample in the teflon beaker to about 10 ml.
- 7.2.8 Add 100 ml 16 M HNO_3 and boil to remove the HCl.
- 7.2.9 Evaporate the sample to a volume of about 50 ml.

- 7.2.10 Remove from the hotplate, and add a volume of distilled water equal to the volume of the sample.
- 7.2.11 Add 8 M HNO_3 to a volume of 150 ml, 1 g of H_3BO_3 and allow the solution to cool.
- 7.2.12 Filter the solution through a Whatman GF/A glass fiber filter and wash the filter a few times with 8 M HNO_3 . Discard any residue in the filter paper and proceed with the analysis of the filtrate according to step 7.3.1.

7.3 Anion Exchange Separation

- 7.3.1 To the solution from the coprecipitation procedure or from the acid dissolution which should be 7-9 M in nitric acid, add 1g of NaNO_2 , heat to boiling and cool.
- 7.3.2 Pass the sample solution through the prepared anion exchange resin column (cf. Section 5.3.4) at a flow rate no greater than 4 ml/min.
- 7.3.3 After the sample has passed through the column, rinse the column with six column volumes of 8 M HNO_3 , again at a flow rate no greater than 4 ml/min.
- 7.3.4 Rinse the ion exchange resin column with six column volumes of 12 M HCl at a flow rate no greater than 2 ml/min.
- 7.3.5 Elute the plutonium with four column volumes of 12 M HCl containing 1 ml of 1 M NH_4I per 30 ml of the 12 M HCl , at a flow rate no greater than 2 ml/min.
- 7.3.6 Rinse the column with two portions of 12 M HCl equal to the volume of the column of resin at maximum flow rate.
- 7.3.7 Evaporate the sample containing the plutonium to about 20 ml and add 5 ml of 16 M HNO_3 .

7.3.8 Evaporate the sample to near dryness.

7.3.9 Add 20 ml of 16 M HNO₃ and evaporate to near dryness.

7.4 Electrodeposition

7.4.1 Add 2 ml of a 5% solution of NaHSO₄ · H₂O in 9 M H₂SO₄ to the sample.

7.4.2 Add 5ml of 16 M HNO₃, mix well and evaporate to dryness, but do not bake.

7.4.3 Dissolve the sample in 5 ml of the preadjusted electrolyte (cf. section 5.3.7), warming to hasten the dissolution.

7.4.4 Transfer the solution to the electrodeposition cell using an additional 5-10 ml of the electrolyte in small increments to rinse the sample container.

7.4.5 Add three or four drops of thymol blue indicator solution. If the color is not salmon pink, add 1.8 M H₂SO₄ (or 1.5 M NH₄OH) until this color is obtained.

7.4.6 Place the platinum anode into the solution so that it is about 1 cm above the stainless steel slide which serves as the cathode.

7.4.7 Connect the electrodes to the source of current, turn the power on, and adjust the power supply to give a current of 1.2 amps. (Constant current power supplies will require no further adjustment, but others may require further adjustments during the electrodeposition).

7.4.8 Continue the electrodeposition for a total of 1.5 to 2.0 hours.

7.4.9 When the electrodeposition is to be terminated, add 1 ml of 15 M NH₄OH and continue the electrodeposition for 1 minute.

- 7.4.10 Remove the anode from the cell and then turn off the power.
- 7.4.11 Discard the solution in the cell and rinse the cell 3 times with 1% NH_4NO_3 in 0.15 M NH_4OH .
- 7.4.12 Disassemble the cell and wash the slide with ethyl alcohol that has been made basic with NH_4OH .
- 7.4.13 Touch the edge of the slide to a tissue to absorb the alcohol from the slide.
- 7.4.14 Dry the slide, place it in a box and label for counting.

7.5 Alpha Pulse Height Analysis

- 7.5.1 When the amount of Pu-238 is large compared to the amount of Pu-239 and/or Pu-242, and when the amount of Pu-239 is large compared to the amount of Pu-242, tailing can contribute to the counts in the lower energy peaks. When this occurs, it is necessary to make corrections. One way of making these corrections is to prepare Pu-238 and Pu-239 sources in the same manner in which the samples are prepared, and determine the corrections from the alpha spectra of the pure isotope.
- 7.5.2 Background corrections of course must also be made. The background should be determined by at least a 4000 minute count and preferably longer if possible.
- 7.5.3 Count the samples for at least 1000 minutes, or longer if the detector efficiency is less than 15%, if the tracer yield is low, or if the unknown plutonium activity is low.
- 7.5.4 Determine the total counts in the Pu-238, Pu-239 and Pu-242 energy regions, and make the background and tailing corrections if necessary.

8. Calculation of Results

8.1 Calculation of Plutonium Concentrations

The concentration of plutonium-239 or plutonium-238 in the aliquot of water taken for analysis is given by:

$$X_i = \frac{C_i \times SA_t \times V_t}{C_t \times V_s} \quad (8.1)$$

where X_i = the concentration of plutonium-239 or plutonium-238 in the water in disintegrations per minute (d/m) per liter.

C_i = the net sample counts in the plutonium-239 or plutonium-238 energy region of the alpha spectrum.

SA_t = the specific activity of the Pu-242 tracer in d/m/ml.

V_t = the volume of the Pu-242 tracer added in ml.

C_t = the net sample counts in the plutonium-242 tracer energy region of the alpha spectrum.

V_s = the volume in liters of the water sample taken for analysis.

8.2 Calculation of Alpha Spectrometer Efficiency

The absolute counting efficiency of the alpha spectrometer, ϵ , must be determined in order to calculate the plutonium recovery of the analytical procedure.

To determine this efficiency requires a standard source of a known alpha particle emission rate:

$$\epsilon = R_s / R_\alpha \quad (8.2)$$

where R_s = the net counting rate of the standard source in the energy region of the alpha emitter of interest in counts per minute.

R_{α} = the absolute alpha particle emission rate
of the alpha emitter of interest in alphas
per minute.

8.3 Calculation of Plutonium Recovery of the Chemical Analysis

The plutonium recovery efficiency expressed as a fraction, E, will be given by:

$$E = \frac{(C_t/t)}{SA_t \times V_t \times \epsilon} \quad (8.3)$$

where t = the counting time in minutes

and the other terms are as defined in sections 8.1 and 8.2.

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