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*Title:* Separation and Purification of Plutonium and Uranium from Cloth Swipes, Vegetation and Soil Samples

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# Separation and Purification of Plutonium and Uranium From Cloth Swipes, Vegetation and Soil Samples

by

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## INTRODUCTION

We have developed techniques for separating plutonium and uranium from cloth swipes, vegetation and soil samples. The swipes are dissolved in strong mineral acids. The vegetation and soil samples are autoclaved to comply with U S Department of Agriculture regulations, dried to constant weight, ashed in a muffle furnace and dissolved with strong mineral acids. Soil samples are sterilized and the uranium and plutonium are leached from the soils' surfaces with aqua regia. The plutonium and uranium are separated and purified by a series of anion exchange columns prior to analyses by thermal ionization mass spectroscopy (TIMS).

## SAMPLE PREPARATION

**Swipes** - Place swipes in 100 ml Teflon beakers and add 10 ml of 16 M $HNO_3$ and 25 ml of 12 M $HClO_4$. Add 2 ng of $^{242}Pu$ tracer and 150 ng of $^{233}U$ tracer. Place on a hot plate set at 215 °C and evaporate to dryness. Remove the beakers from the hot plates and cool to room temperature. Add 10 ml of 12 M $HClO_4$ to each sample and re-evaporate to dryness.

**Vegetation** - Seal the vegetation samples in autoclave bags and sterilize in accordance with the autoclave manufacturer's directions. Transfer the sterilized vegetation samples into tarred 1000 ml beakers and place in a 110 °C drying oven until constant weight is obtained. Transfer 10 -100 gram aliquots of dried vegetation to 1000 ml quartz beakers and place in a muffle furnace. Ash the vegetation samples at 550 °C for 24 hours. (The ashing rate can be controlled by placing covers over the beakers. Continue the ashing process until all of the carbon in the samples is oxidized.) Transfer the ash to 100 ml Teflon beakers and add 20 ml of 16 M $HNO_3$ and 40 ml of 12 M $HClO_4$. Trace each sample with 2 ng of $^{242}Pu$ tracer and 150 ng of $^{233}U$ tracer. Place on hot plates set at 215 °C and evaporate to dryness. Remove the beakers from the hot plates and cool to room temperature. Add 25 ml of 12 M $HClO_4$ to each sample and re-evaporate to dryness. Dissolve each sample in 30 ml of 8 M $HNO_3$ and transfer to plastic 40 ml centrifuge tubes. Centrifuge at 2000 rpm for 5 minutes. Transfer the supernates to 100 ml Teflon beakers. Add 30 ml of 8 M $HNO_3$ to each centrifuge tube, mix thoroughly and centrifuge at 2000 rpm for 5 minutes. Add the rinses to the Teflon beakers and evaporate to dryness.

**Soils** - Seal the soil samples in autoclave bags and sterilize the samples in accordance with the autoclave manufacturer's directions. Transfer 1 gram aliquots of soil to 100 ml Teflon beakers. Add 2 ng of $^{242}Pu$ tracer and 150 ng of $^{233}U$ tracer to each sample. Slowly add 30 ml of 16 M $HNO_3$. (Foaming may be prevented by adding a few drops of

n-octyl alcohol.) After any reactions have subsided add 10 ml of 12 M HCl. Allow the mixture to react at room temperature for an hour. Heat the solutions on hot plates set at 215 °C until the volumes are reduced to approximately 20 ml. Transfer the solutions to 40 ml plastic centrifuge tubes and centrifuge at 2000 rpm for 5 minutes. Transfer the supernates to clean 100 ml Teflon beakers. Add 30 ml of 16 M $HNO_3$ to each centrifuge tube, mix thoroughly and transfer the acids and residues back into the first set of Teflon beakers. Add 10 ml of 12 M HCl and repeat the nitric-hydrochloric leach for another hour with heating and stirring. (Add nitric acid as required to maintain the volume above 20 ml.) Cool to room temperature. Transfer the solutions to the 40 ml plastic centrifuge tubes and centrifuge at 2000 rpm for 5 minutes. Add the supernates from the second leaches to those obtained from the first leach cycle. Place on hot plates set at 215 °C and evaporate the samples to soft dryness. Cool to room temperature. Add 20 ml of 29 M HF and 20 ml of 12 M $HClO_4$ and evaporate to soft dryness. Add 5 ml of 12 M $HClO_4$ to each beaker and warm to dissolve the samples. Transfer the samples to 40 ml quartz centrifuge tubes and evaporate the samples to dryness by heating over a Meeker burner. Flame the sides of the quartz tubes thoroughly to remove any residual hydrofluoric acid. Cool to room temperature, add 5 ml of 8 M $HNO_3$ and evaporate to soft dryness.

## URANIUM AND PLUTONIUM SEPARATION PROCEDURE

1. Add 5 ml of 8 M $HNO_3$ to each swipe, vegetation or soil sample and evaporate to near dryness, i.e., less than 0.5 ml.

2. Dissolve the samples in 5 ml of 8 M $HNO_3$.

3. Pass the solutions through the large anion exchange columns that have been pre-conditioned with 10 ml of 8 M $HNO_3$.

4. Rinse the containers with 3 ml of 8 M $HNO_3$ and pass the rinses through the columns.

5. Rinse the columns with two separate 3 ml aliquots of 8 M $HNO_3$. Allow the columns to drain completely between each addition.

6. Elute the uranium fractions into clean 100 ml Teflon beakers by passing 30 ml of 8 M $HNO_3$ through each column. Place the solutions on hot plates set at 215 °C and evaporate to dryness.

7. Elute the plutonium fractions into a clean 40 ml glass centrifuge tubes by passing 10 ml of 0.5 M HCl and 10 ml of HI-HCl solution through the columns. Place the solutions on hot plates set at 215 °C and evaporate to dryness.

## PLUTONIUM PURIFICATION PROCESS

8. Add 2 ml of aqua regia to the plutonium fractions collected in step 8 and evaporate to dryness.

9. Add 1 ml of 0.1 M $H_2SO_4$ to each tube to dissolve the plutonium.

10. Load the samples onto small anion-exchange columns that have been preconditioned with two 1 ml aliquots of 0.1 M $H_2SO_4$.

11. Rinse the tubes with 1 ml of 0.1 M $H_2SO_4$ and add the rinses to the columns.

12. Rinse the columns with two 1 ml portions of the $H_2O_2$-HCl solution. Rinse the tips of the columns with a stream of deionized water. Discard the eluants.

13. Rinse the columns with two 1 ml portions of the HF-HCl solution. Rinse the tips of the columns with a stream of deionized water. Discard the eluants.

14. Rinse the columns with three 1 ml portions of 12 M HCl. Discard the eluants.

15. Elute the plutonium fractions into 40 ml glass centrifuge tubes with three 0.5 ml additions of HI-HCl reagent. Allow the columns to drain completely between each addition.

16. Evaporate the solutions to dryness.

17. Add 6 drops of $HNO_3$ to each sample and evaporate to dryness. Add 6 drops of 12 M HCl to each sample and evaporate to dryness.

18. Dissolve the samples in 1 ml aliquots of $H_2O_2$-HCl solution and load onto small anion exchange chromatography columns that have been pre-conditioned with two 1 ml aliquots of the $H_2O_2$-HCl solution. Rinse the tubes with 1 ml aliquots of the $H_2O_2$-HCl solution and pass the rinse through the columns. Wash the columns with 2 ml of 8 M $HNO_3$. Rinse the tip of each column with deionized water and discard the eluants.

19. Elute the plutonium into clean 10 ml quartz test tubes using three 1 ml additions of concentrated HBr. Allow each HBr addition to drain completely before adding the next.

20. Slowly evaporate the HBr to dryness.

21. Add 4 drops of $HNO_3$ and 4 drops of $HClO_4$ to each sample. Heat at 130° C for one hour. Raise the temperature to 180° C and continue evaporating to dryness.

22. Add 10 drops of 12 M HCl to each sample and slowly heat on a heat block until dry. Cool to room temperature.

23. Visually inspect the samples for signs of residue. If any residue is detected inside the test tubes, repeat steps 19 through 23.

24. Submit the samples for mass spectrometric analyses.

## URANIUM PURIFICATION PROCESS

25. Add 2 ml of aqua regia to the uranium fractions collected in step 6 and evaporate to dryness.

26. Add 1 ml of 0.1 M $H_2SO_4$ to dissolve the uranium.

27. Load the samples onto small anion-exchange chromatography columns that have been pre-conditioned with two 1 ml aliquots of 0.1 M $H_2SO_4$. Rinse the containers with 1 ml of 0.1 M $H_2SO_4$ and add the rinses to the columns.

28. Rinse the columns with two 1 ml additions of $H_2O_2$-HCl reagent. Allow the columns to drain completely between each $H_2O_2$-HCl addition. Discard the eluants.

29. Rinse the columns with two 1 ml portions of the HF-HCl solution. Rinse the tip of each column with a stream of deionized water. Discard the eluants.

30. Rinse the columns with three 0.5 ml additions of HI-HCl reagent. Allow the columns to drain completely between each addition. Rinse the columns with 20 drops of 8 M HCl.

31. Elute the uranium from the small anion exchange chromatography columns into clean 40 ml quartz centrifuge tubes with 1 ml aliquots of 1 M $HNO_3$ and 1 ml aliquots of 16 M $HNO_3$. Evaporate to soft dryness. Add 6 drops of 12 M HCl and evaporate to dryness.

32. Dissolve the samples in 1 ml aliquots of $H_2O_2$-HCl reagent and load on smal anion exchange chromatography columns that were prepared with two 1 ml aliquots of the $H_2O_2$-HCl solution.

33. Use one additional 1 ml portion of $H_2O_2$-HCl reagent to rinse the tubes from step 32. Pass the rinses through the anion exchange columns.

34. Rinse the columns with 15 drops of 6 M HCl.

35. Elute the uranium from the columns into clean 40 ml quartz centrifuge tubes with three 1 ml portions of Type I reagent grade water.

36. Transfer aliquots containing 50 ng of uranium into clean 10 ml quartz test tubes and evaporate to dryness. (Assume 50% chemical yield for this procedure.)

37. Add 4 drops of 16 M $HNO_3$ and 4 drops of 12 M $HClO_4$. Heat at 130° C for one hour. Raise the temperature to 180° C and continue evaporating to dryness.

38. Add 10 drops of 12 M HCl and slowly heat on a heat block until dry. Cool to room temperature.

39. Visually inspect the samples for signs of residue. If the samples do not contain any residue, submit for mass spectrometric analyses. If any residues are detected inside the test tubes, proceed with step 40.

40. Dissolve the sample in 1 ml of 8 M $HNO_3$.

41. Load the samples on small anion exchange chromatography columns that have been pre-conditioned with two 1 ml aliquots of 8 M $HNO_3$. Rinse the columns with two 1 ml aliquots of 8 M $HNO_3$.

42. Elute the uranium fractions into 10 ml quartz test tubes with 6 ml aliquots of 8 M $HNO_3$. Place test tubes in heating blocks and evaporate to dryness.

43. Add 1 ml 12 M HCL to the test tubes and place in a 110 °C heating block until dry.

44. Repeat steps 37 through 39.

**REAGENTS**

$^{242}Pu$ Tracer calibrated to NIST SRM Pu 949f.
233U Tracer calibrated to NIST SRM U-960
$HClO_4$: 12 M
$HNO_3$: 16 M, 8 M,, 2 M, 1 M
HBr: 47% (unstabilized)
HI: 48% (unstabilized)
HCl: 12 M, 8 M, 6 M, 0.5 M
Aqua regia: 3:1 mixture, by volume, of 12 M HCl and 16 M $HNO_3$
HI-HCl mixture: 1:9 mixture, by volume, of 48% HI and 12 M HCl
$H_2O_2$-HCl reagent: 2 drops of 30% $H_2O_2$ to 10 ml 12 M HCl
HF-HCl reagent; 0.06 M HF in 12 M HCl

Prepare the large anion exchange chromatography columns by placing 3 ml of AG MP-1, 50-100 mesh, anion exchange resin in BIO-RAD Polypropylene Econo-Column Chromatography columns.

Prepare small anion exchange chromatography columns by placing AG MP-1, 50-100 mesh, anion exchange resin in disposable automatic pipettor tips that are 7-cm-length by 5-mm-diameter. Place plugs of prewashed quartz wool in the automatic pipettor tips and add resin to a depth of 2 cm.

Bio-Rad macroporous anion exchange resin: AGMP-1, 50 to 100 mesh. This resin is pretreated by warming overnight in a mixture of 50% 12 M HCl and 50% Type 1 reagent grade water. It is washed 20 times with Type 1 reagent grade water and stored as an aqueous slurry in Teflon bottles.