RFP-2955

MASTER

CONF-791049--15

ANALYSIS OF ROCKY FLATS SOILS FOR SIX RADIONUCLIDES BY A SEQUENTIAL METHOD

J.R.Stevens, D.R.Guhlow, T.F.Rees, and K.J.Grossaint. Analytical Laboratories, Rockwell International, Golden, Colorado, USA.

ABSTRACT

A dramatic increase in soils analysis for actinides has occurred at the Rocky Flats nuclear facility in recent years. Intensive investigation of the extent of potential contamination of soils was needed to generate a valid data base for evaluating the true environmental impact of plant operations.

A method for the sequential analysis of Rocky Flats soils for six actinides of interest was developed to facilitate the large number of radionuclide analyses. The isotopes determined were: U-238, U-235, U-234, Th-232, Th-230, Th-228, Np-237, Pu-239/240, Am-241, and Cm-244. The method included addition of tracer isotopes for each actinide, pyrosulfate fusion to help solutize minerals and decompose organic matter, sequential separation by cation and anion exchange techniques, extraction into thenoyltrifluoroacetone (TTA)/organic phase, and subsequent counting of alpha activity by pulse height analysis. The efficiency of recovery for tracer isotopes ranged from 40% for curium, to 95% for plutonium. The detection limits for the method were determined at 0.2 disintegrations per minute per gram (DPM/g) of soil for thorium, uranium, neptunium, and plutonium. The limits were a factor of three higher (0.6 DPM/g) for americium and curium, primarily because of inefficient extraction of these components by TTA. The sequential analysis was developed into a routine laboratory procedure to be used when multi-element soil analyses were requested.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

INTRODUCTION

The emphasis on "Low as Practicable" pollutant emission limits for nuclear facilities such as Rocky Flats sometimes places a strain on laboratories performing the analyses required for a monitoring effort. In the case of radioactive isotope analyses, public concern may have a major impact on the monitoring effort.

For a facility such as Rocky Flats, where on-site contamination of soils has occurred, the monitoring effort has a great significance. Analyses performed to determine the extent of contamination contributed by plant operations are complicated by the presence of low levels of fall-out activity, and also by the natural radioactivity prevalent in the plant environs. Natural radioactivity in soils surrounding Rocky Flats is very significant, as illustrated by the presence of several high-grade ore Uranium mines in the front range, not too distant from the plant.

The responsibility for the soil monitoring program at Rocky Flats lies with the Environmental Studies Group, which is a part of the Health, Safety, and Environment Organization. That group defines the sampling program and sampling techniques for soils, as well as the other myriad analyses required by Environmental Protection Agency (EPA), state regulatory agencies, Department of Energy (DOE), and plant self-imposed, regulations or emission limits.

The Analytical Laboratory provides a significant portion of the analytical support for the soil monitoring program. We also support an extensive research and development effort at Rocky Flats, which is developing processes for decontaminating soils.

We found that although not requested for every sample, analysis for the six radionuclides plutonium, americium, uranium, thorium, neptunium, and curium, was requested often enough to put a severe strain on our ability to meet a reasonable time scale for reporting results. As a response to this realization, a method was developed to permit sequential separation of those six nuclides from only four aliquots of soil.

EXPERIMENTAL

The chemical form of environmental radionuclides cannot be known with certainty, in most cases. It is therefore necessary to rigorously treat the sample for dissolution, both to be certain of complete chemical dissolution, and to convert to the expected soluble species, prior to the separation steps. We desired a procedure which used a minimum of hydrofluoric acid, because of its influence on the ion exchange separation of certain actinides (1-3). Our studies have indicated that prior treatment of the sample by fusion with potassium pyrosulfate greatly aided in attaining complete dissolution of radionuclide contaminants in soil. An added advantage may be the chemical breakdown of humus, vegetative debris, or other organic material present in the soil sample. This is definitely an advantage to us, considering the hazards of perchloric acid digestion, or other possible digestion techniques.

Analysis Procedure - Preparation of the Sample

The procedure followed to obtain the sequential separation of the six nuclides was as follows:

Sieve the sample through a standard 10-mesh screen.

Determine the weight fraction of fines to coarse particles.

Dry the less-than-10-mesh fines at 100°C, to constant weight. (Determine the wet-to-dry weight ratio).

Grind the dry fines to a homogeneous powder, using an analytical mill.

Muffle the ground soil at 500°C for 24 hours.

Cool, re-weigh to determine weight loss.

Homogenize by tumbling 10 minutes.

> NOTE: Rocky Flats experience is that the preponderance of the activity is associated with the less-than-10-mesh fines (Particularly contaminant plutonium). If a more complete inventory is desired, the greater than 10-mesh fraction should be analyzed alongside the fines.

Weigh separate, appropriately sized sample aliquots into four clean platinum beakers or Pyrex® glass beakers.

Thoroughly mix each aliquot with potassium pyrosulfate powder, in a ratio of one part sample to three parts pyrosulfate, by weight.

Add known amounts of tracer isotopes U-232, Pu-236, and Am-243 activity to three of the aliquots. If possible, the tracer count rate should be approximately equal to the expected sample activity for the corresponding element.

Add known amounts of tracer isotopes Np-237, Th-232 and/or Th-228, and cm-244 to the fourth aliquot.

Dry, and fuse each aliquot over the flame of a laboratory burner, for a period of 10-15 minutes.

Remove from heat and cool. Take care that the sample is not lost by breakage of the glass beaker during the fusion and cooling steps.

Analysis Procedure - Separation of Americium and Curium

Dissolve the fused sample in a minimum of 0.5 N HNO_3. Note that an insoluble residue of approximately 1-10% by weight may remain.

Filter through Whatman 540® filter paper, rinsing with 0.5 N, ? until the filtrate volume is about 25 ml.

Prepare a 50W-X8, 50-100 mesh, hydrogen form resin column, about 6 cm high.

Condition the column with one column volume (CV) of 0.5 N HNO_3.

Elute the sample filtrate through the column, collecting the effluent in a clean beaker. Rinse the column with two CV of 0.5 N HNO_3, adding the rinse effluent to the original.

Set the collected effluent aside for later separations of Pu, Th, Np, and U.

Strip the Americium and Curium from the column with one CV of 8 N HNO_3, one CV of 16 N HNO_3, then another CV of 8 N HNO_3, collecting the strip effluent in a clean beaker.

Evaporate the strip effluent to dryness, dissolved in 12 N HCl, evaporate to dryness, and re-dissolve in 12 N HCl.

Add approximately 0.5 g of ammonium iodide, and set aside for 10 minutes.

Prepare an ion exchange column containing 3 cm of 1-X4 Bio-Rad® resin, rinsing with 12 N HCl.

Pour the sample through the column, collecting the effluent in a clean beaker.

Evaporate the effluent to dryness, add 16 N HNO_3, evaporate to dryness, and repeat. On the third evaporation, use caution to take the sample to just past incipient dryness.

Dissolve the residue in a minimum of 0.1 N HNO_3, and transfer to a 4-dram vial, using a total of about 5 ml of 0.1 N HNO_3.

Add 0.5 ml of pH=5 ammonium acetate buffer, and 5 ml of 0.5 M TTA in xylene.

Shake the mixture on a Burrell wrist action shaker for approximately 15 minutes. Let stand to separate phases.

Transfer the (top) organic phase as quantitatively as possible onto a 3-cm stainless steel planchet, evaporate to dryness, flame at red heat, and count the Am and Cm alpha activity on a pulse height analyzer. Multiple extractions may be useful to increase the chemical recovery of the americium and curium. Typical first extraction recoveries range from near 10 to about 50%.

Analysis Procedure - Separation of Thorium and Plutonium

Add an equal volume of 16 N HNO_3 to the effluent collected from the Am and Cm separation, to make that solution approximately 8 N HNO_3.

Elute the sample through the column, collecting the effluent containing uranium and neptunium in a clean beaker. Set aside for further separation.

Strip the thorium from the column with 3 CV of 9 N HCl, collecting in a clean beaker.

Strip the plutonium from the column with 5 CV of 0.4 N HNO_3/ 0.1 N HF, collecting in a clean beaker.

Evaporate the thorium strip solution to incipient dryness, and convert to the nitrate form with 16 N HNO_3. Evaporate to dryness a second time, and redissolve in 5 ml of 0.1 N HNO_3.

Transfer the redissolved thorium strip solution to a 4 dram vial containing 5 ml of 0.5 M TTA in xylene, and shake on a Burrell wrist action shaker for 15 minutes. Let stand to separate phases. Quantitatively transfer the organic phase to a planchet, evaporate, flame, and count the thorium alpha activity by pulse-height-analysis.

Evaporate the plutonium strip solution to incipient dryness, redissolve in 1 N HNO_3, and transfer to a 4-dram vial.

Add 5 ml of 0.5 M TTA in xylene and 0.1 g of sodium nitrite.

Shake for 15 minutes, and transfer the organic phase as before, prior to counting the plutonium alpha activity by pulse-height analysis.

Analysis Procedure - Separation of Uranium and Neptunium

Evaporate the effluent containing neptunium and uranium to dryness, and convert to the chlorides with 12 N HCl. Evaporate to incipient dryness a second time and redissolve in 12 N HCl.

Add ammonium iodide and hydroxylamine hydrochloride. Set aside for 10 minutes.

Prepare an ion exchange column containing 3 cm of 1-X4, 100-200 mesh, chloride form resin.

Condition the column with 12 N HCl.

Elute the sample through the column, discarding the effluent.

Strip the neptunium from the column with 3 CV of 4 N HCl/0.1 N HF, collecting in a clean beaker.

Strip the uranium from the column with 2 CV of water, collecting in a clean beaker.

Evaporate the neptunium strip solution to dryness, redissolve in 16 N HNO_3, and evaporate to incipient dryness. Redissolve in 0.5 N HNO_3.

Add 0.1 g ferrous chloride ($FeCl_2$) and 0.1 g hydroxylamine hydrochloride. Let stand for 10 minutes.

Transfer to a 4 dram glass vial, add 5 ml of 0.5 M TTA in xylene, and shake for 15 minutes on a Burrell wrist action shaker.

Quantitatively transfer the organic phase to a planchet as before, prior to counting the neptunium alpha activity by pulse-height-analysis.

Evaporate the uranium strip solution to dryness and redissolve in 8 N HNO_3. Evaporate to incipient dryness and redissolve in 0.1 N HNO_3.

Transfer to a 4 dram vial with approximately 5 ml of 0.1 N HNO_3. Add 1 ml of pH 5 ammonium acetate buffer. Add 5 ml of 0.5 M TTA, and shake for 15 minutes on a Burrell wrist action shaker. Let stand to separate the phases.

Quantitatively transfer the organic phase to a stainless steel planchet, evaporate, flame, and count the uranium alpha activity by pulse-height-analysis.

Analysis Procedure - Chemical Recoveries

The sequential procedure requires four aliquots of each soil sample because of the necessity of adding activity of the same isotope analyzed for, in the case of curium and neptunium. We had no supply of alpha-emitting isotopes of these elements, except Cm-244 and Np-237.

The other four radionuclides' chemical recovery was monitored with isotopes known to be absent in Rocky Flats soils.

For 75 test samples of Rocky Flats soils, the chemical recoveries were as follows:

	Ave(%)	Range(1)
Americium(2)	50	
Curium(2)	40	
Thorium	80	
Plutonium	95	
Neptunium	60	
Uranium	60	

(1) Lowest recovery experienced, high recovery experienced.

(2) May include one, two, or three successive extractions.

Although not spectacular, these chemical recoveries were achieved on analyses performed on a routine basis, by non-degreed technicians, on soils of variable composition, and under pressures of time.

The manhours of effort to perform the sequential analyses was approximately 24 hours per sample. This compares with approximately 43 hours per sample average estimated for doing the analyses on separate aliquots.

The calculated limits of detection for the radionuclides, based upon these chemical recoveries, the aliquot size (approximately one quarter gram), and the counting efficiencies of our detector system were 0.2 disintegrations per minute per gram for thorium, plutonium, neptunium and uranium.

Table 1. Sequential Method Chemical Recoveries, and Agreement between Replicate Separations, for 75 Test Samples of Rocky Flats Soils.

Acti~~o~~nide	Chemical Recovery(1) Ave (%)	Range	Sample Count Agreement (3 Planchets)
Americium	50(2)	8-64	± 12%
Curium	40(2)	11-55	± 47% (3)
Thorium	80	16-90	± 11%
Plutonium	95	12-104	± 9%
Neptunium	60	6-88	± 26%
Uranium	60	21-87	± 14%

(1) Lowest ~~percent~~ recovery observed and highest recovery observed, for the set of samples.

(2) May include one, two or three successive extractions.

(3) Large value because of the counting statistic error for acti~~o~~nides with activity near the detector background.

The limit of detection for americium and curium were calculated at 0.6 disintegrations per minute per gram, primarily because of the difficulties encountered in the extraction step for these elements.

These limits of detection approximate the level expected for plutonium from fall-out in soils in the area surrounding the Rocky Flats facility.④

References

1.

2.

3.

4.

5.

Soil Sampling Procedure

The procedure for sampling soils at Rocky Flats is specified by an internal document.

The criteria for sampling include:

A. Area chosen
    1. open, relatively flat area

10 A RFP-2955

1. IPST Cat. No. 2057, Analytical Chemistry of Elements Series, Analytical Chemistry of Uranium, translated from the Russian, N. Kramer, 1963 Israel Program for Scientific Translations Ltd., S. Monson, Jerusalem, Israel, and Daniel Davey and Co., Inc., New York, 1963.

2. Complex Compounds of Transuranium Elements, translated from the Russian, C. N. Turton and T. I. Turton, Consultants Bureau Enterprises, Inc., New York, 1962.

3. Anion Exchange Studies of the Fission Products, K. A. Kraus and F. Nelson, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Wol. 7, pp. 113-125, United Nations, New York, 1956.

4. Plutonium Determination in Soil by Leaching and Ion-Exchange Separation, N.Y. Chu, Analytical Chemistry, Vol. 43, pp. 449, 1971.

5. D. D. Hornbacher, Private Communication. Environmental Control and Analysis, Energy Systems Group, Rockwell International, Rocky Flats Plant, Golden, Colorado. August, 1979.

2. undisturbed location during the time interval of interest
3. no excessive run-off during heavy rains
4. no mechanical disturbance of soil evident
5. only light to moderate vegetation

B. Collection procedure

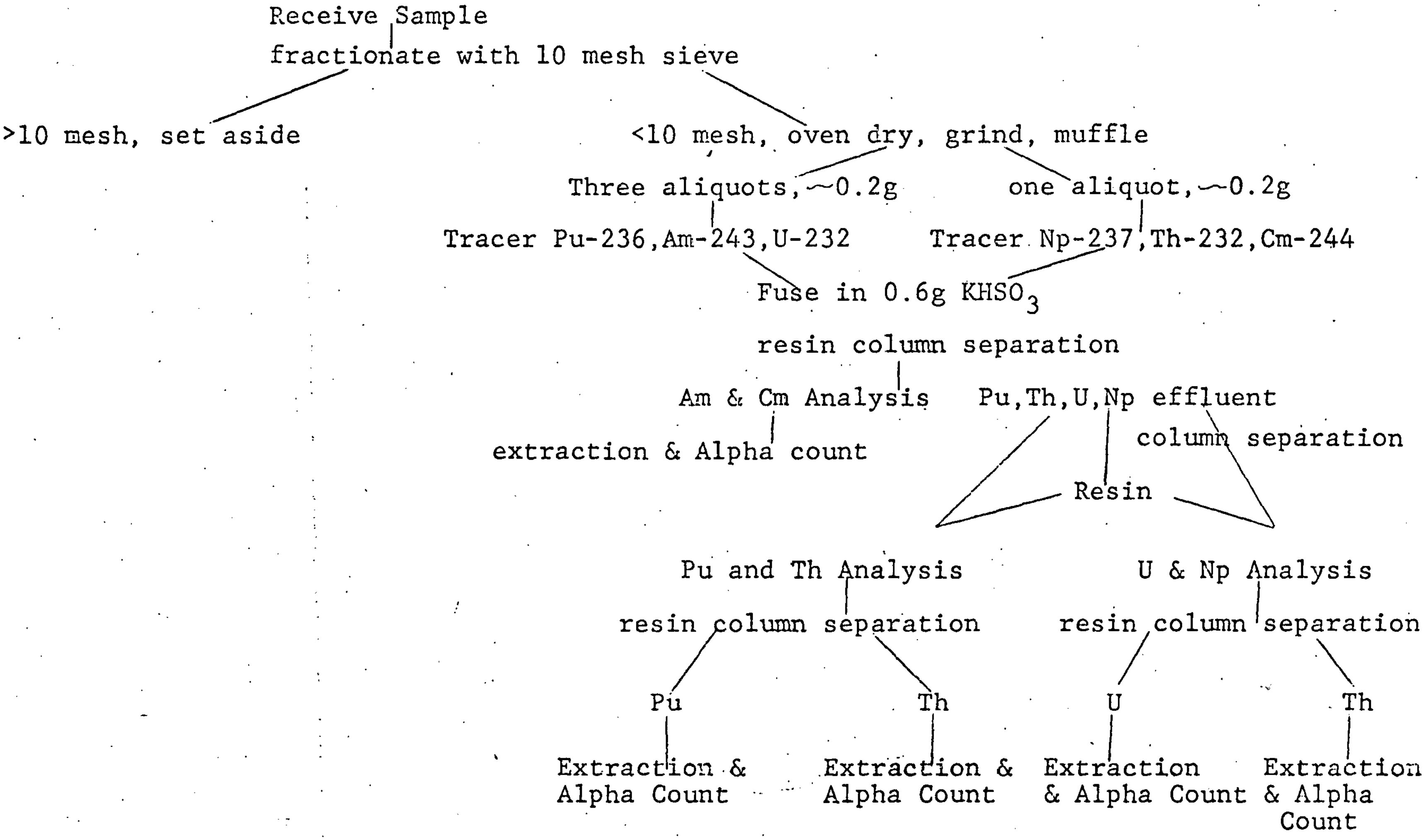
Normal samples-five samples (10 x 10 x 5 cm). One at center, one at four compass points a specified distance from center, composited.

Resuspendible-1 cm depth, all soil particles less than two millimeters analyzed.

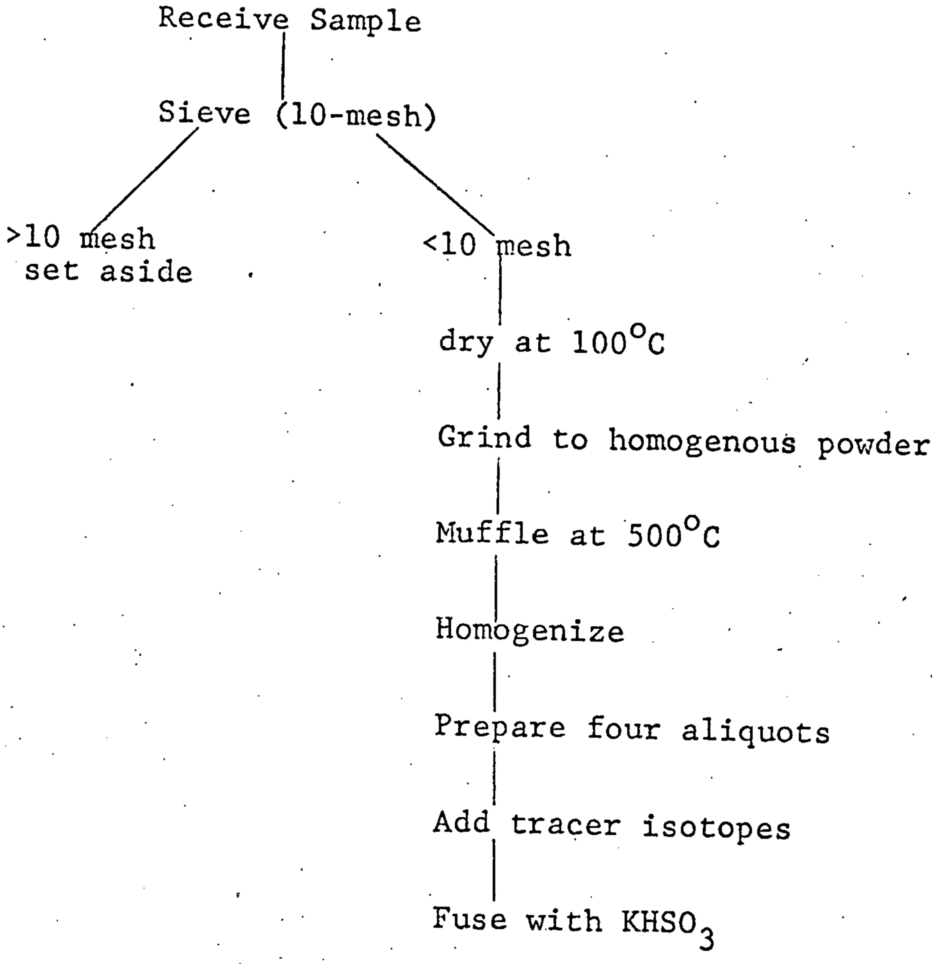
Special (care)-use an orchard auger, 8.3 cm. diameter barrel.

Profile-motorized backhoe to dig trench, (60 to 120 cm) samples taken from walls after all loose soil is removed.

OVERALL SCHEME FOR SEQUENTIAL ANALYSIS



SOIL SAMPLE PREPARATION



SEPARATION OF Am AND Cm

Dissolve fused sample in 0.5 N HNO_3

filter off approximately 1 to 10% residue remains

prepare 50W-X8, 50-100 mesh hydrogen form column

condition column with 0.5 N HNO_3

collect effluent for later separation of
Pu, u, Th, and Np

strip Am and Cm with 8 N HNO_3, 16 N HNO_3, 8 N HNO_3

convert to chloride with 12 N HCl

adjust oxidation state of iron (NH_4I)

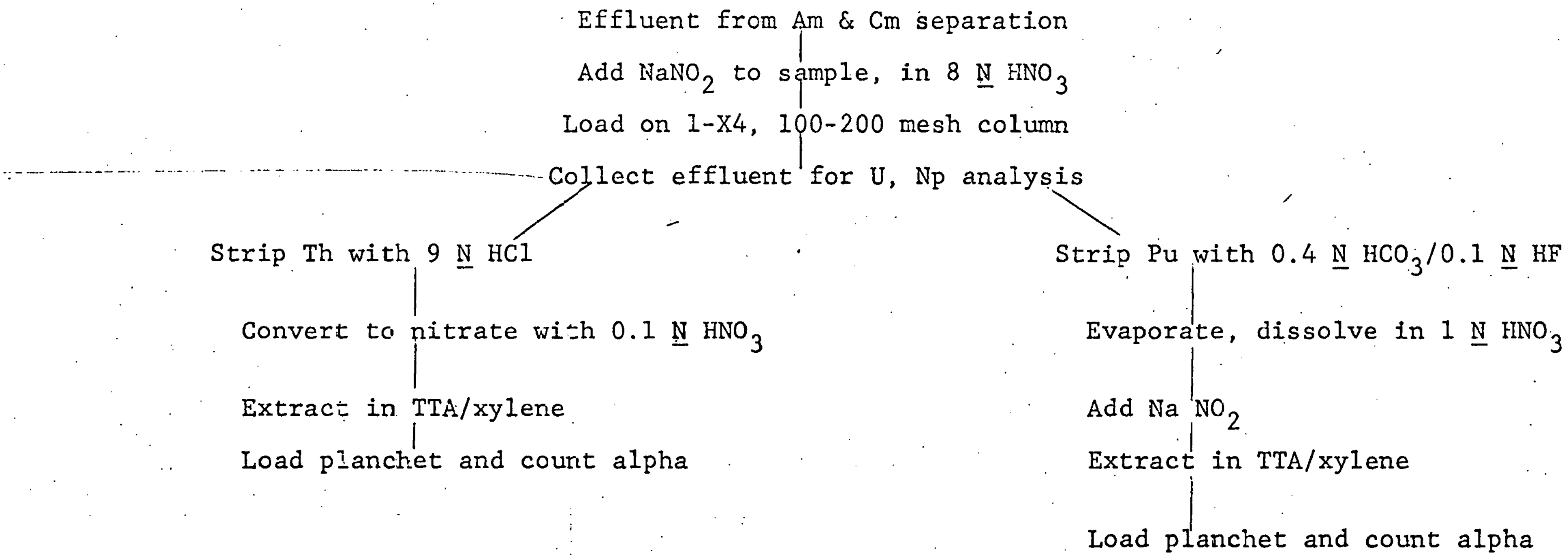
prepare 1-X4 column, condition with 12 N HCl

resin column separation

extract from buffered (pH=5) HNO_3 with TTA, re-extract

load planchet with organic flame, count alpha on PHA

SEPARATION OF THORIUM AND PLUTONIUM



SEPARATION OF URANIUM AND NEPTUNIUM

Effluent from Pu & Th separation

Convert to chloride with 12 N HCl

Add NH_4I & $HONH_2$ HCl, wait 10 minutes

Condition 1-X4, 100-200 mesh, column with 12 N HCl

Elute sample, discard effluent

Strip Np with 4 N HCL/0.1 N HF

- convert to nitrate (16 N HNO_3)
- dissolve in 0.5 N HNO_3
- adjust oxidation state with $FeCl_2$, HNOH·HCl
- extract into TTA/xylene
- load planchet and count alpha

Strip U with water

- convert to nitrate (8 N HNO_3)
- dissolve in 0.1 N HNO_3
- extract from pH5 buffer with TTA/xylene
- load planchet and count alpha

slides accompany copy no. 1 –
please return with manuscript