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ATOMIC ENERGY OF CANADA LIMITED

L'ÉNERGIE ATOMIQUE DU CANADA LIMITÉE

SEQUENTIAL ANALYSIS OF SELECTED ACTINIDES IN URINE PART I

Analyse séquentielle de certains actinides dans l'urine 1ère Partie

G.H. KRAMER

Paper presented at the 25th Annual Bioassay Conference,
Las Vegas, 1 November, 1979

Chalk River Nuclear Laboratories Laboratoires nucléaires de Chalk River

Chalk River, Ontario

July 1980 juillet

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Résumé

Le contrôle médical du personnel au moyen d'analyses d'urine dans les cas de contamination possible par des actinides a nécessité le développement et la mise en application d'un programme analytique qui permettra de séparer et d'identifier les radionucléides émetteurs alpha de ces éléments. Les travaux actuels concernent Pu, Am et Th. Ces éléments sont extraits d'échantillons cendrés d'urine par coprécipitation et échange ionique. L'analyse finale consiste à galvanoplastifier les actinides et les compter au moyen d'un spectromètre à rayons alpha. La récupération moyenne de ces éléments dans l'urine est la suivante: Pu 64%, Am 74% et Th 69%.

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ABSTRACT

The monitoring of personnel by urinalysis for suspected contamination by actinides necessitated the development and implementation of an analytical scheme that will separate and identify alpha emitting radionuclides of these elements. The present work deals with Pu, Am and Th. These elements are separated from an ashed urine sample by means of coprecipitation and ion exchange techniques. The final analysis is carried out by electroplating the actinides and counting in a α-spectrometer. Mean recoveries of these elements from urine are: Pu 64%, Am 74% and Th 69%.

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1. INTRODUCTION

The development of new fuels and their possible recycling in the nuclear power industry, makes it essential that a comprehensive actinide analysis of environmental and biological samples be available to identify radionuclides that may have escaped to the environment, or which may be excreted by humans following accidental intakes. The literature contains many methods that deal with actinide analysis from various media. Many of them are specific, usually for plutonium (1-3), and are thus unsuitable for a sequential analysis and identification procedure. Other methods do not deal with the complete range of actinides (4,5) nor can they be easily extended to include the missing members.

A method has been developed that, at present, will separate and identify thorium, plutonium and americium in urine. It is flexible enough to allow separation and identification of curium, neptunium and uranium to be added at a later date.

Urine samples from selected employees are routinely analysed in our laboratory for alpha emitting actinide contamination but until now a chemical procedure to identify the individual elements present has not been developed.

Unfortunately, urine is a very complex material to work with. It is composed of inorganic salts, inorganic complexes and organic compounds. The 50 elements present in a normal urine sample (6), collected over a 24 hour period will weigh, after removal of water and organic material, approximately 33 grams.

It is necessary for an analytical scheme to be able to clearly separate 2 x 10^{-14} grams or less of an actinide of interest. This weight would, in the case of ^{241}Am, correspond to 2.5 mBq/ 24 hour urine sample. This is the level at which a person would be removed from work that may involve further actinide contamination (13).

A survey of the literature has shown that ion exchange techniques are the most applicable to the problem. Under certain conditions the actinides can be quantitatively retained on an anion exchange column whilst most other elements are washed through (7-9).

One of the difficulties in urinalysis is the ashing step by which the urine is converted to an inorganic salt solution. Organic compounds must be removed, otherwise large reductions in recovery would result from formation of complexes. The conventional wet and dry ash methods are time consuming and one runs the added risk of forming refractory oxides during the dry ash step. This is to be avoided to maintain high recoveries. A new ashing method has been developed which is complete in less than 2 hours and does not exceed 400°C, the formation of refractory PuO_2 is thus minimized as is reflected by the recoveries.

The actinides are concentrated by a ferric hydroxide precipitation (so removing Group 1 metals) and passed through an anion exchange column. Thorium and plutonium are eluted separately and electroplated in preparation for alpha spectrometry. The americium is purified by elution from a second anion exchange column in non-aqueous media, plated and counted. The scheme is illustrated in Figure 1.

The stable element "contamination" at various points in the analytical scheme has also been investigated. Early results were a great asset in obtaining high decontamination factors in order to achieve reasonably consistent and high recoveries.

2. EXPERIMENTAL

2.1 Apparatus

Alpha spectrometry was carried out in Canberra vacuum chambers at 4 Pa using Ortec ruggedized silicon surface barrier detectors (2.3 cm^2). Pulse height analysis was performed with a Nuclear Data ND 100 multichannel analyser, an NDC 560 analog to digital converter and an ND 508 gated analog router. The system is interfaced with a teletype.

Bio-Rad AGI X8 100-200 mesh anion exchange resin is used in all columns.

2.2 Ashing Procedure

Depending on the urgency of obtaining the results of an analysis either method 'a' (slow) or 'b' (fast) may be used.

a) The urine sample is placed in a Griffon beaker of 2 to 3 times the volume of the sample. Concentrated nitric acid (10% to 20% of the sample volume) is added* and the beaker is heated, covered by a 'speedyvap" lid, until the sample boils briskly. The heat is adjusted to maintain a constant controlled boiling and as the solution evaporates more concentrated nitric acid is added* until the solution becomes light in colour. The solution is evaporated to dryness (the residue must not be baked in case insoluble residue form) and more concentrated HNO_3 is added* dropwise until the residue is covered by liquid. This procedure is repeated as many times as necessary to obtain a pale yellow residue. It is unusual for it to be white. The hot residue is moistened with concentrated HNO_3 and distilled H_2O is slowly added until the solids have dissolved. The final solution should be clear and almost colourless. This procedure can take up to 24 hours to complete.

* Additions of nitric acid must be made with care. It is necessary to perform the operation in a fume hood.

b) The urine is placed in a large evaporating dish (22 cm diameter) and evaporated to almost dryness. Fuming nitric acid is added* to the hot mixture until a clear orange solution is obtained. The solution is evaporated to almost dryness whilst constantly washing the sides of the dish with more fuming nitric acid (1-2 mL at a time). The mixture in the dish will begin to char and finally self-ignite and almost all the organics will be consumed. The dark brown residue is treated with more fuming nitric acid whilst being heated. The residue should be heated until brown fumes just begin to form and at this point fuming nitric acid is added dropwise to the dish. This is continued until the residue is either white or very pale yellow. The residue is dissolved in nitric acid and centrifuged to remove silica. The silica residue has not been found to contain any measurable activity from spiked samples analysis. This ashing procedure takes 1.5 to 2 hours to complete.

2.3 Separation Sequence

1. Ferric chloride (100 mg) is added to the nitric acid salt solution which results from the ashing procedure. The solution is neutralized with concentrated aqueous ammonia and an excess added. The insoluble hydroxides and phosphates are allowed to settle from a hot solution. The solution is allowed to cool to room temperature.

2. The precipitate is separated by centrifuging and is washed with distilled water, recentrifuged and dissolved in 2 to 3 mL of concentrated nitric acid - supernatants being discarded in each step. Eight molar (M) nitric acid is added to make a final solution of 30 to 50 mL and more concentrated nitric acid is

* This procedure is hazardous and must be carried out in a fume hood. Protective clothing is advised.

added, if necessary to ensure $[HNO_3] \geq 8$ M. This solution is treated with sodium nitrite (0.5 g) and boiled immediately for 1 to 2 minutes to remove gaseous nitrogen compounds. When the solution is cool, it is passed through column one (see below) at 1 to 2 mL/min flow rate.

3. Americium and the majority of elements are eluted by 20 column volume (CV) of 8 M nitric acid. Reserve the elute for step 6.

4. Thorium is eluted with 10 CV of 8 M hydrochloric acid. This fraction is ready for electroplating - see below.

5. Plutonium is eluted with 10 CV of 8 M hydrochloric acid and 0.05 M NH_4I. This fraction is ready for electroplating - see below.

6. The eluate from step 3 is neutralized with excess concentrated aqueous ammonia and the precipitate allowed to settle from hot solution until the mixture reaches room temperature. The mixture is centrifuged and the precipitate is washed with distilled water, recentrifuged and finally redissolved in 2 to 3 mL of concentrated nitric acid - supernatants being discarded in each step.

7. The nitric acid solution is diluted with distilled H_2O and the pH adjusted to 1.5 ± 0.2. This pH is not critical but if it is too low the oxalates will not precipitate and if it is too high the phosphates will precipitate. The solution is heated and an equal volume (~50 mL) of saturated $(COONH_4)_2$ is added. The solution is allowed to stand overnight.

8. The mixture is centrifuged and the precipitate is washed with distilled water and recentrifuged - supernatants being discarded in each step. The precipitate is dissolved in 2 to 3 mL of concentrated nitric acid (cautiously warmed if necessary) and

enough methanol added to ensure 93% methanol content (usually ~50 mL) ammonium nitrate is also added so that $[NH_4NO_3] \geq 0.2$ M.

9. The solution is passed through column two (see below) at a flow rate of 1 to 2 mL/min. The column is washed with 20 CV 1 M nitric acid (93% methanol) and the americium is eluted with 10 CV 1 M nitric acid. This fraction is ready for electroplating - see below.

2.4 Electropolishing Procedure

The stainless steel discs (1.9 cm diameter) are electropolished prior to the electroplating procedure and stored under distilled water if necessary. The electropolishing solution is prepared by dissolving 200 g citric acid in 200 mL water and adding 58 mL 18 M sulphuric acid. The discs are cleaned in this solution for about 30 to 40 seconds at 2 A with the stainless steel disc as the anode.

2.5 Electroplating Procedure

Figure II shows the cell configuration. Prior to electroplating, 2 mL of 5% w/v sodium bisulphate are added to the sample and the resulting solution is evaporated to a small volume (1-2 mL) and 5 mL of aqua regia are added. The solution is heated to dryness and the residue again treated with aqua regia and evaporated to dryness. The residue is fumed with two 5 mL portions of concentrated hydrochloric acid which leaves a white residue. The beaker is cooled and the residue dissolved in 4 mL 15% w/v sodium sulphate disodium EDTA solutions. The plating solution is introduced into the cell (see diagram) and the beaker washed with two 3 mL portions of disodium EDTA solution which are also added to the cell. The cell is operated at 0.5 A for 3 hours. In the case of thorium, 1 mL saturated ammonium oxalate is added to the cell in place of 1 mL EDTA solution.

2.6 Ion Exchange Columns

Enough resin is used to give a column volume of ~5 mL in a column of internal diameter of 1.0 cm. The resin is first slurried in distilled H_2O and introduced into the column. Column one is prepared for use by washing with 10 CV of 8 M nitric acid.

Column two is prepared for use by washing with 10 CV of 8 M nitric acid followed by 10 CV of 1 M nitric acid (93% methanol).

Column two is a water jacketed column and is operated at 23°C.

2.7 Multi-element analysis

This work was performed by the General Chemistry branch using an Inductively Coupled Plasma Atomic Emission spectrometer manufactured by Jobin Yvon, France.

2.8 Notes for Use of Method

i. If americium is the only element desired, begin with step 7. In step 9, the americium should be eluted with 8 M nitric acid.

ii. If thorium is the only element desired, then steps 5 to 9 may be omitted.

iii. If plutonium is the only element desired, then steps 6 to 9 may be omitted.

iv. Sometimes there appears to be an insoluble residue in step 2. This may be removed by centrifuging the sample solution with no detriment to the subsequent separation.

3. RESULTS AND DISCUSSION

The method was first tried by spiking ashed urine samples with ^{239}Pu, ^{241}Am and natural thorium (0.17 Bq). The recoveries of these radionuclides is shown in Table I. The poor and erratic

recoveries of thorium could not be explained but was thought to be due to the plating procedure. This step was modified to that described above and the results for plating thorium from water solution are given in Table II. Other workers have reported that amounts of ^{232}Th in excess of 100 µg have interfered with most electroplating procedures (10). The role of the oxalate in reducing this interference is not yet well understood, but is obviously effective. The continuing interference of some element in the electroplating is illustrated in Table II for Trials 10 and 11. The thorium yield has dropped significantly despite the fact that the spike was added just prior to electroplating. The cause is not yet known.

As a further test to the method, five urine solutions were spiked with the three radionuclides and allowed to equilibrate for several days. The results of the analysis are shown in Table III. Typical α-spectra are shown in Figures III and IV and as can be seen cross contamination is negligible, thus allowing a positive identification of the radionuclide contamination of urine. The presence of ^{224}Ra etc. in Figure IV is due to ingrowth following separation. It is evident that radium is satisfactorily removed during the separation procedure.

The stable element interferences were investigated by doing several blank runs with urine samples. The elemental composition of urine is shown in Figure V and at least 28 elements exceed 100 µg (Al, B, Br, Ca, Co, Cd, Cl, F, Fe, Ge, K, Li, Mg, Mn, Mo, Nb, Na, P, Pb, Si, S, Sn, Te, U, Zn, Zr) which could give rise to serious interference. A flow diagram, Figure V illustrates the elements detected at various points in the procedure, and Table IV gives the quantitative contaminations of the fractions of interest. On the basis of this information, the method was altered to its present form mainly by increasing the volume of column washes. Further multi-element analysis showed a significant

improvement of up to an order of magnitude decrease in the elements given in Table IV. The difficulty in complete separation was illustrated by examining the ion exchange characteristics of Ca^{2+} (a major contaminant). A sample of calcium nitrate containing approximately 180 mg (the normal content of urine) was eluted through an anion exchange column in the method described above. Calcium is reportedly not adsorbed on an anion exchange resin from either hydrochloric acid (11) or nitric acid (7) and so should be washed through. The results are illustrated in Figure VI, and it can be seen that although calcium has an effective zero distribution coefficient on the resin under the experimental conditions, the massive tail-off from the column could, if undetected, seriously inhibit subsequent analytical steps. The experimental procedure as described removes calcium, and presumably other elements with very low distribution coefficients, to a concentration level of 3.5 mg/L which should be acceptable for further steps. Previously the method was using half the volume for column washing which would give rise to a contamination of 30 to 40 mg/L.

According to the literature (see references 1-5, 7-9 as example), the only elements that should be adsorbed to an appreciable extent on the anion exchange column under the conditions used (8 M nitric acid) are: Th(iv), Pa(v), U(vi), Np(iv), Pu(iv), Au(iii), Pu(iii) and Bi(iii). When the eluant is changed to 8 M hydrochloric acid only Pa(v), U(vi), Np(iv), Pu(iv), Au(iii), Pd(iii), and Bi(iii) should remain. Thus theoretically it should be possible to completely separate the actinides from all other elements. In practice this is not true unless one is willing to use large quantities of eluants which will be very time consuming.

In the case of americium, a similar situation occurs. The distribution coefficients of the actinides from 1 M nitric acid - 93% methanol are given in Table V. Other elements like Ag, Al,

Cu, Cd, Co, Cu, Cs, Fe, Hf, K, Li, Mg, Mn, Ni, Na, Sr, Ti, U, Y, Zr and Zn are not adsorbed (9) but Ba, La, Ce, Nd, Pr, Yb, Pb and Bi are all strongly bound on the column. Fortunately, most of these elements do not occur in urine and Ba, Pb and Bi have not been found in the americium fraction. The contaminants can be seen from Figure V to be calcium and magnesium and a number of other elements. By increasing the column wash only calcium and magnesium were subsequently detected (Ca (4.5), Mg (< 0.05) mg/L).

In all cases the increased wash volumes helped improve yields and the quality of the electroplated sources. The average source is now a pale blue to yellow colour, whereas before the increase in column wash, the plates were black and non reflective.

In principle the separation of actinides is not difficult but the practical difficulty of obtaining clean separations necessitates the use of relatively large volume column washes which are time consuming. The procedure at present takes 3 days to obtain the identity of a given actinide in urine. To improve the cleanliness of separation larger column washes and a longer analysis time would be necessary and at the present time this is thought to be impractical.

4. ACKNOWLEDGEMENTS

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TABLE I

% RECOVERIES OF ^{241}Am, ^{239}Pu AND NATURAL THORIUM FROM ASHED URINE SAMPLES

TRIAL	^{241}Am	Nat_{Th}	^{239}Pu
1	80.	17.	82.
2	96.	15.	57.
3	78.	52.	94.
4	95.	29.	55.
5	105.	90.	95.
6	78.	54.	68.
mean	89.	43.	75.
st. dev.	11.	28.	18.

TABLE II

QUANTITY OF THORIUM PLATED FROM WATER BY THE NEW PROCEDURE

TRIAL	AMOUNT Th ADDED µg	% AMOUNT Th RECOVERED
1	13.	103.
2	13.	93.
3	25.	96.
4	38.	104.
5	38.	75.
6	316.	98.
7	316.	68.
8	632.	95.
9	632.	99.
10[a]	13.	66.
11[a]	13.	62.

[a] Thorium spike added to the 8 M HCl wash during a urine separation.

TABLE III

% RECOVERIES OF ^{241}Am, ^{239}Pu AND NATURAL THORIUM FROM URINALYSIS

TRIAL	^{241}Am	Nat_{Th}	^{239}Pu
1	83.	102.	55.
2	60.	66.	65.
3	66.	51.	52.
4	87.	60.	83.
5	74.	70.	64.
mean	74.	70.	64.
st. dev.	11.	19.	12.

TABLE IV

STABLE ELEMENT CONTAMINATION OF THE FRACTIONS OF INTEREST BEFORE INTRODUCING MORE COLUMN WASHES

Fraction	
Th	Al(<1.0) Cu(0.1) Cr(0.18) Ca(4.70) Mg(2.32) Fe(1.42) Si(2.0)
Pu	Al(<1.0) Cu(0.2) Cr(0.18) Ca(0.05) Mg(0.34) Fe(0.85) Si(2.3)
Am	Al(<1.0) Cu(0.15) Cr(0.12) Ca(33.6) Mg(0.49) Fe(0.13) Si(1.3)

Figures in parenthesis are mg/L

TABLE V[12]

DISTRIBUTION COEFFICIENTS OF ACTINIDES ON DOWEX 1X4 FROM 1 M NITRIC ACID - 93% METHANOL

ISOTOPE	Th(IV)	U(VI)	Pu(IV)	Am(III)	Cm(III)
Kd	4×10^4	4×10^2	4×10^3	1.4×10^3	10^3

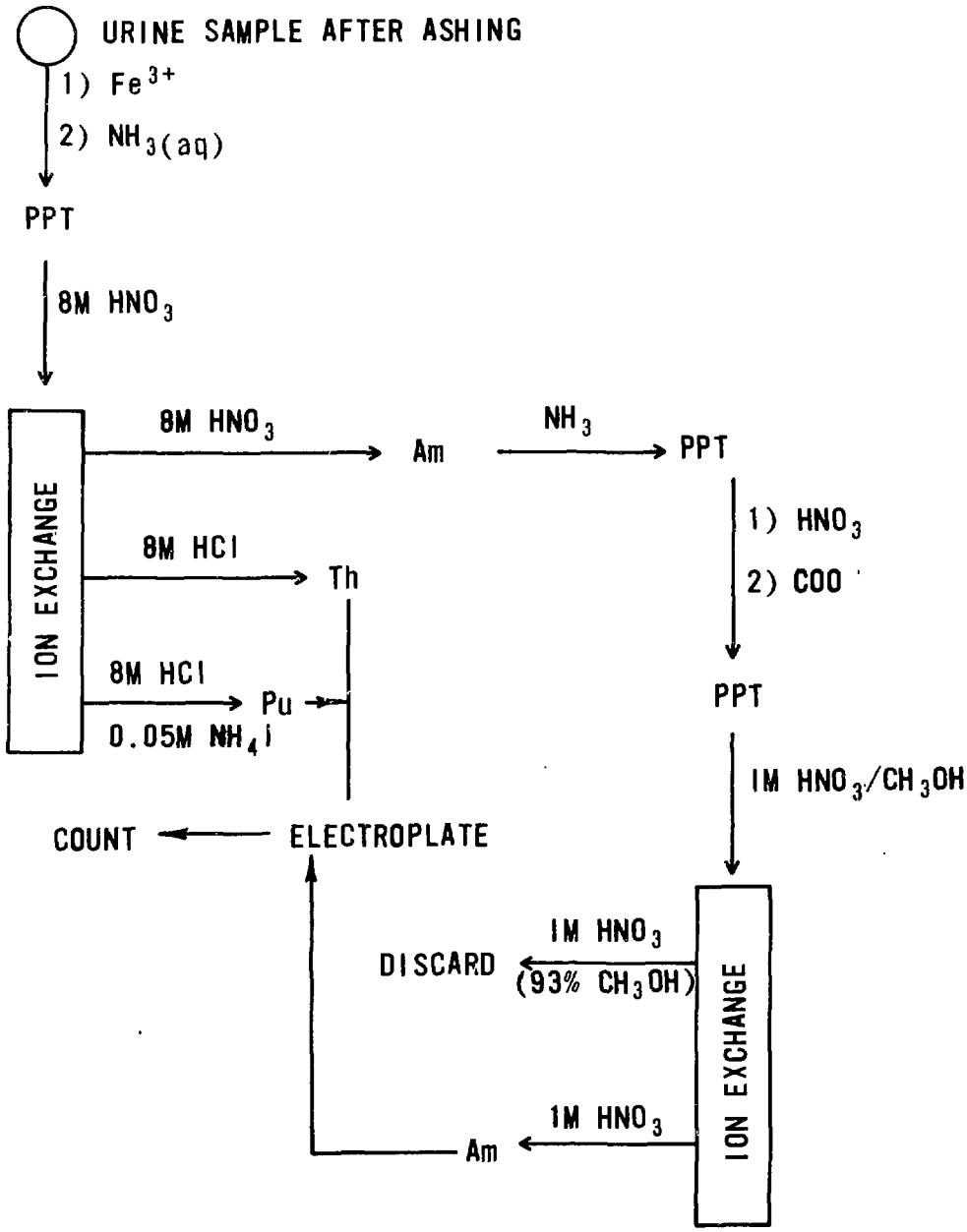

FIGURE I SEQUENTIAL ANALYSIS OF THE ACTINIDES

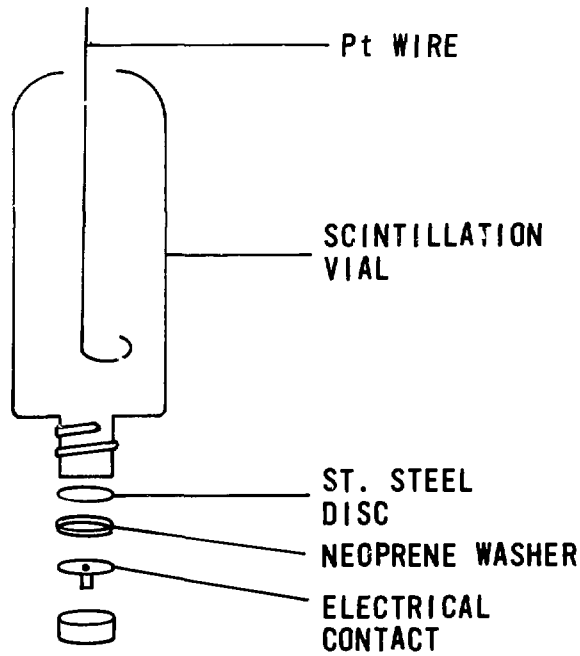

FIGURE II ELECTROPLATING CELL

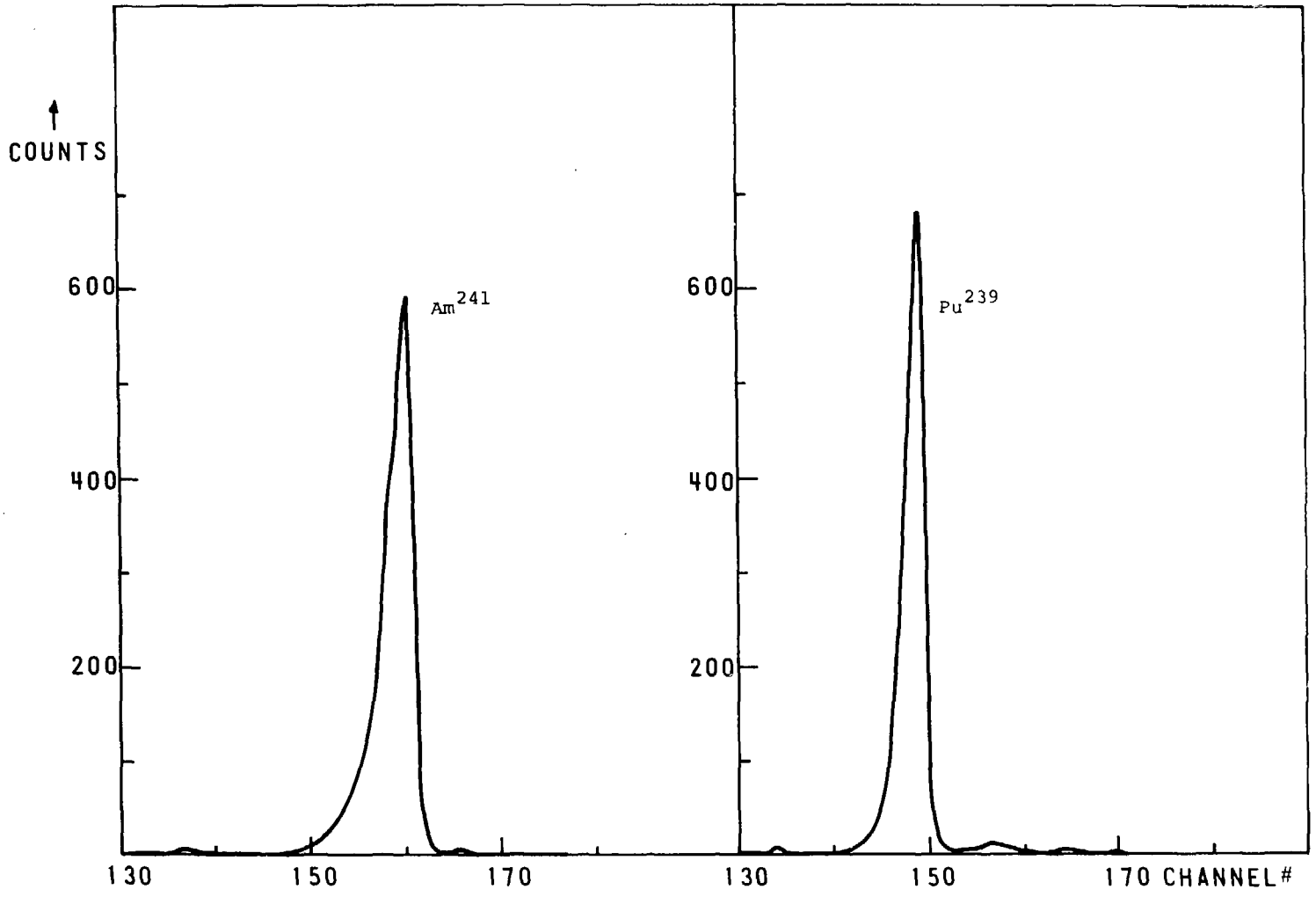

FIGURE III AMERICIUM 241 AND PLUTONIUM 239

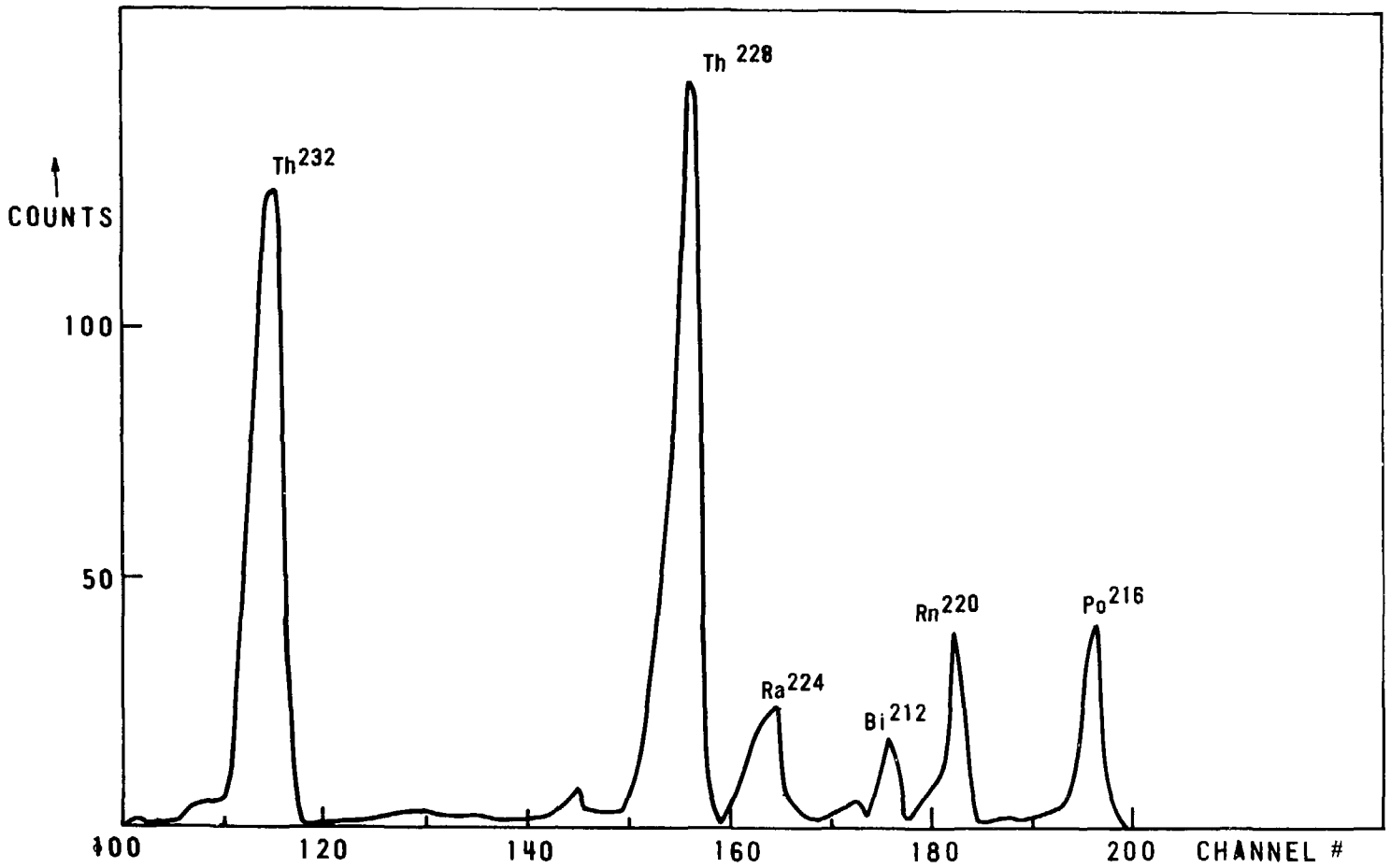

FIGURE IV THORIUM 232

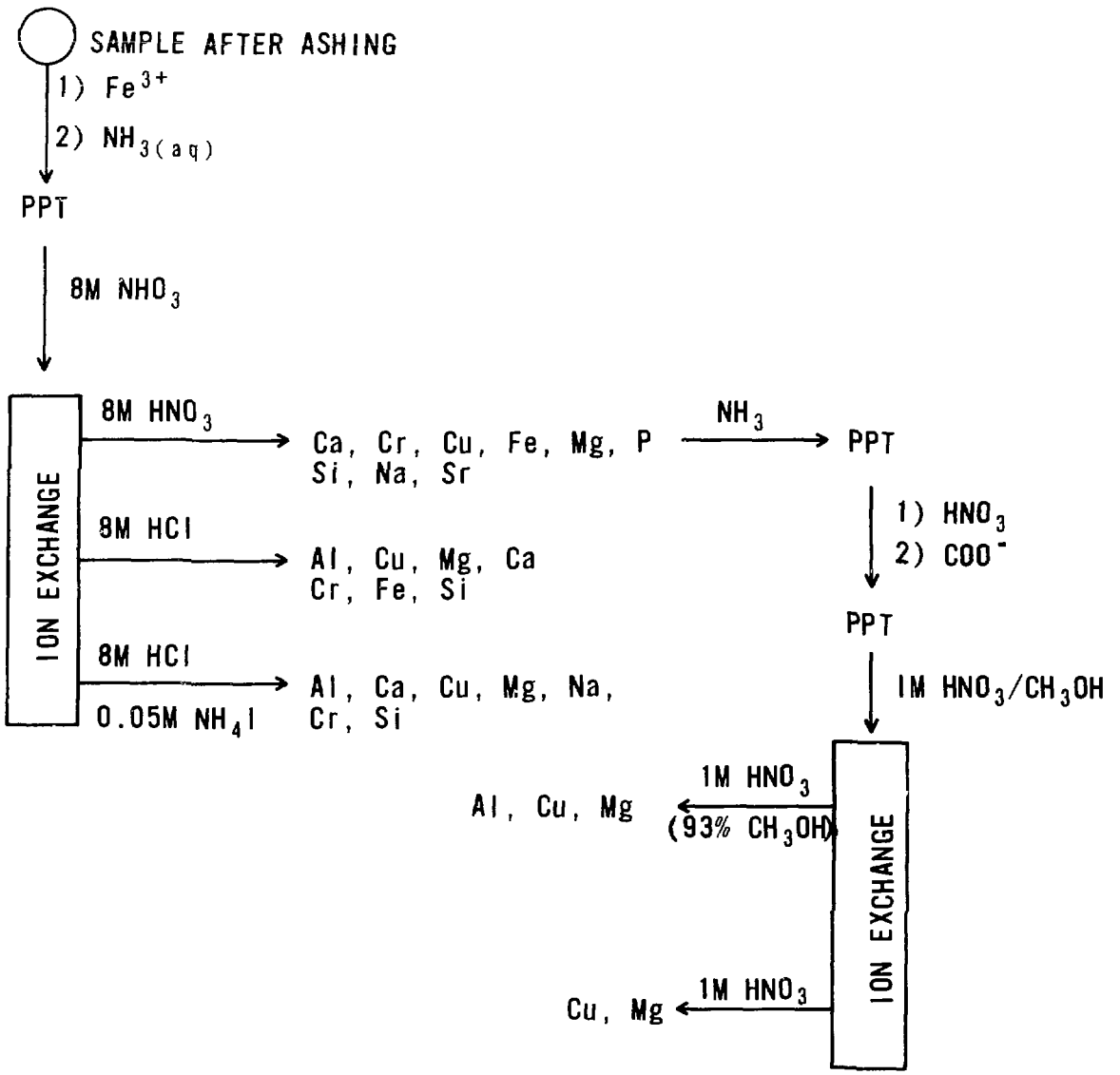

FIGURE V STABLE ELEMENT CONTAMINATIONS

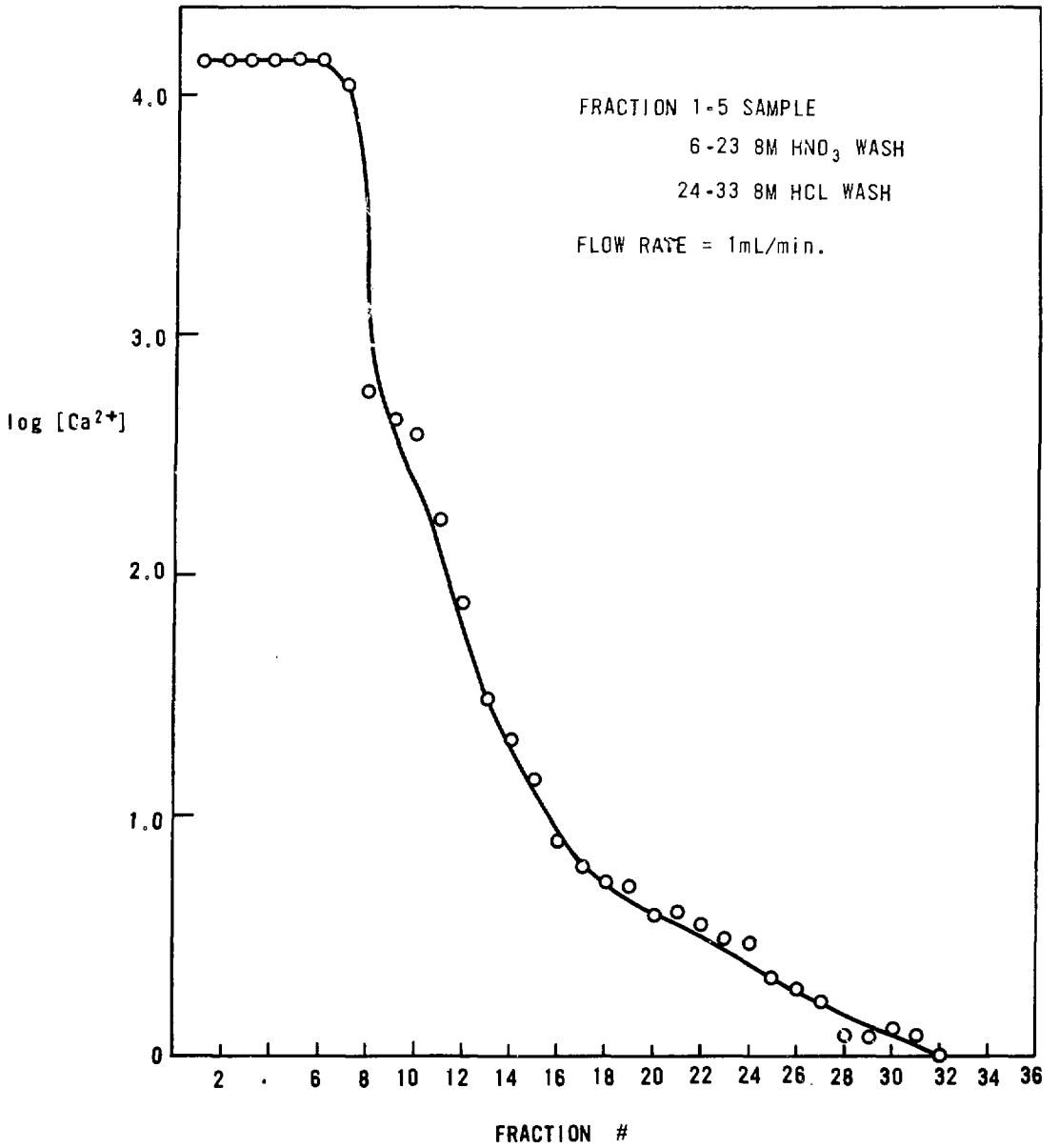

FIGURE VI PLOT Log[Ca^{2+}] AS A FUNCTION OF ELUTION

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