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AEC RESEARCH AND DEVELOPMENT REPORT

DETERMINATION OF NEPTUNIUM-237
IN HUMAN URINE

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A B S T R A C T

A method has been developed for determining neptunium-237 in human urine specimens. The urine is acidified, then concentrated by evaporation. Uranium is removed by a double lanthanum fluoride precipitation using ferrous ammonium sulfate and hydroxylamine hydrochloride as reducing agents. Separation from plutonium is effected by a thenoyltrifluoroacetone extraction using potassium iodide-hydrazine or potassium iodide-hydroxylamine to reduce plutonium to Pu^{+3} and neptunium to Np^{+4} . The trivalent plutonium is not extracted by TTA. Neptunium is stripped from the TTA with HCl and electrodeposited on stainless steel discs from an acid-chloride electrolyte. Recovery of a 200 alpha cpm Np^{237} spike is $87\% \pm 8.5\% \text{ LE}_x$ and of a 1 alpha cpm Np^{237} spike is $80\% \pm 26\% \text{ LE}_x$.

DETERMINATION OF NEPTUNIUM-237 IN HUMAN URINE

The purpose of this investigation was to develop a urinalysis procedure to detect, with reasonable accuracy, 1 alpha cpm Np^{237} in urine specimens. In the initial phase, analytical schemes were evaluated using tracer spikes of approximately 200 alpha cpm Np^{237} because this level of activity was best suited to the electronic alpha counting equipment available. The gamma emitting isotope, Np^{239} , was used in certain cases when a complete material balance through a separation step was desired. As the work progressed, techniques were evaluated at lower spike levels using nuclear film track (autoradiographic) counting techniques^{7/}.

An abundance of literature has been published concerning analysis for neptunium. Roberts^{5/} used nitrate form anion exchange resin, while Wish and Rowell^{8/} used the chloride form. Moore^{3/} utilized a thenoyltrifluoroacetone-xylene extraction. Hyde^{1/} has reviewed many analytical schemes for this element, but none are concerned with urinalysis. Argonne National Laboratory^{2/} describes a procedure for neptunium in urine, but this separation isolates americium, curium, plutonium, thorium, and neptunium as gross alpha. The procedure of Perkins^{4/} for neptunium in urine and the work of Mitchell^{12/} on electrodeposition of the actinides serve as a basis for the work in this report.

Urine media for this investigation was obtained from a composite of routine samples analyzed by the Industrial Hygiene Laboratory. This was stored in a 9-liter carboy and 500 ml portions were siphoned off as needed. The spike used in the evaluation was 96% Np^{237} by alpha energy analysis. The remaining 4% may have been shielded Np^{237} or Th^{230} .

EXPERIMENTAL

Evaluation of Available Procedures

Attempts to analyze urine for Np^{237} following the procedure of Perkins^{4/} gave recoveries of about 50% with poor reproducibility. This procedure separates uranium and plutonium by double lanthanum fluoride precipitation followed by TTA extraction. Ferrous ammonium sulfate and hydroxylamine are used as reducing agents in both steps. Neptunium is stripped from the TTA with 8 N HCl. The HCl is evaporated to a low volume, made alkaline with KOH, and neptunium is electrodeposited on polished stainless steel discs after adding sodium hypochlorite solution.

By using Np^{239} and counting discard fractions from each step of this procedure, it was found that the chemical separations gave 85-90% recovery of neptunium, while the subsequent electroplating procedure was erratic and gave recovery of 15-75%.

The method of R. F. Mitchell^{12/} for electroplating plutonium from an ammonium chloride solution at pH 1 was tried and Np recovery of 30-50% was obtained.

This procedure used a chloride concentration of 0.1-0.2 g/ml, a solution volume of 4-5 ml, and current density of 0.6-1.0 amps/cm². The actinide is transferred to the plating cell with 3 ml 1:2 HCl, neutralized to methyl red with concentrated NH₄OH and acidified with 2 N HCl using two drops excess.

Modification of Mitchell's Plating Procedure

The above procedure (Mitchell) was modified by adding 0.5 ml 12 N KOH to the electroplating cell prior to addition of the sample. One ml aliquots of Np²³⁹-nitrate solution were evaporated to dryness in 15 ml beakers and transferred to plating cells with 2 ml 1:1 HCl. Each solution was neutralized with concentrated NH₄OH then acidified with 1 N HCl using 4 drops excess. This procedure gave 86% recovery in one hour's plating time at 300 ma. One-half hour's plating time at 500-600 ma gave 97% recovery and one hour at this current gave essentially 100% recovery (table 1.)

Perkins' Chemical Separation With Modified Mitchell Procedure

Urine samples spiked with Np²³⁷ and analyzed using Perkins' chemical procedure and the modified Mitchell plating procedure resulted in poor recoveries. This was due principally to shielding of alpha particles by a heavy deposit of iron on the plated disc. Most of the iron originated from the two ferrous ammonium sulfate reductions. An HF wash following the second LaF₃ precipitation effectively reduced iron contamination from this step. Various schemes were tried to prevent iron from coming through the TTA extraction (e.g., nitric acid was substituted for the HCl strip solution, tartaric and citric acids were added during the extraction to complex iron); but none were successful. Therefore, it was necessary to use a reductant which did not contain iron. The combination of potassium iodide and hydrazine was evaluated and found satisfactory.

Evaluation of KI-Hydrazine Reductant

To determine if the KI-hydrazine reduction and the acid-chlorine plating were compatible, 100 alpha cpm Np²³⁷ was added to 50 ml beakers, evaporated to dryness, reduced, extracted and plated. The discs were free of shielding deposit, but recovery was only 50-60%. A grease film was present in the 15 ml beakers in which the 8 N HCl strip from TTA extraction was evaporated. This could prevent quantitative transfer of Np to the plating cell and also reduce plating efficiency. This film was eliminated by using separatory funnels with Teflon stopcocks in place of lubricated glass stopcocks and also by fuming the strip solution residue in the 15 ml beaker with 0.5 ml HNO₃ and 0.5 ml HClO₄ prior to transfer to the plating cell.

An evaluation of the procedure as developed at this point was made by analyzing sixteen 500 ml portions of urine spiked with 180 alpha cpm Np²³⁷. Recovery was 82% ± 15.4% LE_x.

Elimination of Trace Iron By Acidification With HCl

Some of the plated discs from the above evaluation still had a dark deposit presumed to be iron. In general this was more pronounced on discs of lower recovery. There were indications that plated discs from urine which had been acidified with HCl to dissolve solids were free of iron deposit. (One set of four 500 ml aliquots used in the evaluation had come from the 9-liter carboy after concentrated HCl had been added to dissolve an unusual accumulation of precipitated solids.)

To determine the efficacy of the HCl addition, eleven 500 ml portions of urine were initially acidified with 10 ml HCl and 10 ml HNO_3 , spiked with 200 alpha cpm Np^{237} and analyzed. The electroplated discs were of very uniform appearance and were relatively free of shielding deposit. Recovery was $87\% \pm 8.5\% \text{ LE}_x$ (table 2). The HCl is, therefore, beneficial in reducing iron contamination, presumably by degrading iron-containing solids in the original sample so that iron is removed in soluble form during the LaF_3 precipitations and HF wash.

Recovery Using Np^{239}

Thus far, the evaluation has utilized spikes of 40-200 alpha cpm Np^{237} . These relatively large spikes were used because rapid and fairly accurate counting is easily obtained at this level. To show that the technique is equally applicable to smaller amounts of neptunium, four 500 ml portions of urine were spiked with 40,000 gamma cpm using freshly prepared Np^{239} . Activity of Np^{239} is 7.3×10^7 gamma cpm/ug or 5.6×10^{-4} ug/40,000 gamma cpm. By comparison, 5.6×10^{-4} ug Np^{237} would count 0.42 alpha cpm. The recovery was 90% (table 3).

Interference From Uranium and Plutonium

The separation factor for uranium, obtained by this procedure, is at least 1500 to 1. The separation factor for plutonium is greater than 200 to 1. These factors were determined by spiking urine with 1500 and 200 alpha cpm, respectively, of uranium and plutonium, proceeding through the chemical separation, electroplating, and alpha counting. In all cases the discs counted less than 1 cpm above background. No evaluation was made of alpha emitters other than neptunium, uranium and plutonium. Actinium, a usual impurity in lanthanum compounds, is probably eliminated by the TTA extraction since the lanthanum used was not purified to remove alpha emitters and low reagent blanks were obtained (table 4).

Recovery of Low Concentrations of Np^{237}

Spiked samples in the range of 4 alpha cpm and 0.8 alpha cpm along with appropriate urine blanks and reagent blanks were processed and plated. These were counted by a nuclear film track technique⁷ as well as by electronic means.

As seen in table 4, the 4 alpha cpm samples gave good recovery, but the 0.8 alpha cpm recovery was considerably lower. The fact that 4 alpha cpm Np^{237} was 90% recovered and an amount of Np^{239} corresponding in mass to 0.4 alpha cpm Np^{237} was 90% recovered had indicated previously that the procedure was accurate at the 1 alpha cpm level.

KI-Hydroxylamine Reductant

Each step of the procedure was examined separately and it was determined that the loss was in the TTA extraction due to incomplete reduction of neptunium. The KI-hydrazine reduction was re-examined and at the same time evaluation of the KI-hydroxylamine reduction used by Moore² was begun. The latter method afforded satisfactory recoveries at the 1 alpha cpm level (table 5). It was deemed unnecessary to spend additional time on the KI-hydrazine procedure and further work was suspended.

It is for the above reasons that two different techniques, prior to TTA shakeout, are given in the procedure (appendix A). It should be remembered that the KI-hydroxylamine reduction was evaluated at ~ 1 alpha cpm spike level, while the KI-hydrazine reduction was evaluated using 180 and 4 alpha cpm spikes.

SUMMARY

A procedure was developed for determining Np^{237} in urine. Recovery and precision at 200 alpha cpm Np^{237} is $87\% \pm 8.5\% \text{ LE}_x$ and at 1 alpha cpm is $80\% \pm 26\% \text{ LE}_x$. Two slightly different procedures were used at the two levels of alpha activity. Decontamination factors for uranium and plutonium are at least 1500X and 200X, respectively.

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BIBLIOGRAPHY

1. Hyde, E. K., "Separation Methods for the Actinide Elements," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Volume 7, pp 278, 292-297 (1955).
2. Mitchell, R. F., "Electrodeposition of Actinide Elements at Tracer Concentrations," Analytical Chemistry 32, pp 326-328 (1960).
3. Moore, F. L., "Separation and Determination of Neptunium by Liquid-Liquid Extraction," Analytical Chemistry 29, pp 941-944 (1957).
4. Perkins, R. W., A Tentative Bioassay Procedure for the Measurement of Np²³⁷, HW-67067 (1960).
5. Roberts, F. P., An Analytical Method for Neptunium²³⁷ Using Anion Exchange, HW-59032 (1959).
6. Schubert, J., Meyers, L. S., Jr., and Jackson, J. A., The Analytical Procedures of the Bio-Assay Group at the Argonne National Laboratory, ANL-4509 (1951).
7. Schwendiman, L. C., Healy, J. W., and Reid, D. L., The Application of Nuclear Track Emulsions to the Analysis of Urine for Very Low Level Plutonium, HW-22680 (1951)

TABLE 1
ELECTRODEPOSITION OF Np^{237}

<u>Sample</u>	<u>Plating Conditions</u>	<u>γcpm Plated</u>	<u>% Recovery</u>	<u>Average</u>
Std. A	300 ma, 1 hr.	40.0	--	
A-1	" "	33.3	83	
A-2	" "	34.1	85	
A-3	" "	34.8	87	
A-4	" "	36.0	90	86%
Std. B	600 ma, 0.5 hr.	44.6	--	
B-1	" "	41.7	93	
B-2	" "	44.3	99	
B-3	" "	46.1	103	
B-4	" "	41.9	94	97%
Std. C	600 ma, 1 hr.	44.6	--	
C-1	" "	48.5	109	
C-2	" "	45.2	101	
C-3	" "	43.2	97	
C-4	" "	43.7	98	101%

TABLE 2
RECOVERY OF Np^{237} FROM HUMAN URINE
($\text{KI-N}_2\text{H}_4$ REDUCTION)

<u>Sample</u>	<u>α cpm</u>	<u>% Recovery</u>
1	179	88.4
2	172	85.3
3	175	86.5
4	162	80.2
5	169	83.6
6	176	87.3
7	175	86.7
8	175	86.7
9	172	85.1
10	186	92.3
11	184	91.1
Std.	202	
$\bar{x} = 86.7$ $\text{LE}_x = 7.4$ $\% \text{LE}_x = \pm 8.5$		

TABLE 3
RECOVERY OF Np^{239} FROM HUMAN URINE

<u>Sample</u>	<u>γ cpm</u>	<u>% Recovery</u>	<u>Average</u>
Std.	24,566	--	
1	22,653	92.2	
2	21,090	85.8	
3	21,846	88.9	
4	22,487	91.6	89.6%

TABLE 4

DETERMINATION OF Np^{237} IN HUMAN URINE

Sample	Electronic Counting		Autoradiographic Counting	
	Result α cpm	Avg. α cpm	Result α cpm	Avg. α cpm
Reagent Blank (4 determinations)	--	0.07	--	0.04
Unspiked Urine (4 determinations)	--	0.19	--	0.23
Urine + 0.8 α cpm Np^{237}	0.77	0.77	0.68	0.65
" " "	0.80		0.70	
" " "	0.77		0.51	
" " "	0.75		0.72	
Urine + 4.0 α cpm Np^{237}	3.69	3.86	4.00	3.85
" " "	3.55		3.89	
" " "	4.02		3.95	
" " "	4.18		3.55	
Urine + 0.8 α cpm Np^{237} : $(0.77 \alpha\text{cpm} - 0.19 \alpha\text{cpm}) \div 0.8 \alpha\text{cpm} = 73\%$ recovery using electronic counting				
Urine + 0.8 α cpm Np^{237} : $(0.65 \alpha\text{cpm} - 0.23 \alpha\text{cpm}) \div 0.8 \alpha\text{cpm} = 53\%$ recovery using autoradiographic counting				
Urine + 4.0 α cpm Np^{237} : $(3.86 \alpha\text{cpm} - 0.19 \alpha\text{cpm}) \div 4.0 \alpha\text{cpm} = 92\%$ recovery using electronic counting				
Urine + 4.0 α cpm Np^{237} : $(3.85 \alpha\text{cpm} - 0.23 \alpha\text{cpm}) \div 4.0 \alpha\text{cpm} = 91\%$ recovery using autoradiographic counting				

TABLE 5

EVALUATION AT 1 α CPM USING KI-HYDROXYLAMINE REDUCTION

Sample	Gross α cpm	Net α cpm
Std. No. 1	0.96	--
Std. No. 2	0.96	--
Urine Background No. 1	0.06	--
Urine Background No. 2	0.01	--
Urine Background No. 3	0.02	--
Urine Background No. 4	0.02	--
Spike No. 1	0.63	0.60
Spike No. 2	0.76	0.73
Spike No. 3	0.99	0.96
Spike No. 4	0.78	0.75
Spike No. 5	0.82	0.79
Spike No. 6	0.82	0.79
Spike No. 7	0.81	0.78
Spike No. 8	0.80	0.77
Spike No. 9	0.77	0.74
Spike No. 10	0.85	0.82
Average recovery = 80.5%		
$\bar{x} = 0.773$		
$LE_x = \pm 0.20$		
$\%LE_x = \pm 26$		

APPENDIX A

DETERMINATION OF Np^{237} IN HUMAN URINEA. APPARATUS

1. Electrodeposition cells (figure 1).
2. Stainless steel plating discs; 0.50 inch diameter x 0.016 inch thick with a 1.5 microinch finish on one side.
3. Four-position electrodeposition apparatus (figure 2).
4. 100 ml Lusteroid centrifuge tubes.
5. 125 ml separatory funnels with Teflon stopcocks and polyethylene stoppers.

B. REAGENTS

1. Hydrochloric acid; 11.7 N HCl (concentrated), 8 N HCl, 1:1 HCl, 2.0 N HCl, 1.0 N HCl.
2. Hydrofluoric acid; 48% HF (concentrated).
3. Nitric acid; 15.6 N HNO_3 (concentrated).
4. Perchloric acid; 72% HClO_4 (concentrated).
5. Ammonium hydroxide; 15.1 N NH_4OH (concentrated).
6. Chloroform.
7. Ferrous ammonium sulfate; 0.25 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ per ml in distilled H_2O , prepared daily.
8. Hydrazine; 0.4 M N_2H_4 in 2.0 N HCl.
9. Hydroxylamine hydrochloride; 4.0 M $\text{NH}_2\text{OH} \cdot \text{HCl}$, 2.0 M $\text{NH}_2\text{OH} \cdot \text{HCl}$.
10. Lanthanum nitrate; 20 mg La^{+++} per ml in 8 N HNO_3 .
11. Methyl red; 0.04%.
12. Potassium hydroxide; 12 M KOH.
13. Potassium iodide; R.A.C.S. crystalline KI.
14. Thenoyltrifluoroacetone; 0.45 M TTA in benzene, prepared daily.

C. PROCEDURE

1. To 500 ml urine add 10 ml conc. HCl, 10 ml conc. HNO_3 , 40 mg La^{+++} , and a few glass beads. Evaporate on a bare hot plate to about 50 ml and cool.
2. Add 2 ml 2 M $\text{NH}_2\text{OH} \cdot \text{HCl}$, 1 ml Fe^{++} solution, swirl to mix, and transfer to 100 ml Lusteroid centrifuge tube with distilled H_2O to a final volume of ~ 75 ml.

3. Five minutes after addition of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and Fe^{++} , add 5 ml 48% HF to Lusteroid tube, stir, and allow to stand 5 minutes.
4. Centrifuge 10 minutes at 1500 rpm. Decant and discard supernate.
5. Slurry precipitate with 70 ml 1 N HCl. Repeat reduction and precipitation. Centrifuge, decant and discard supernate.
6. Wash inside of tube with 70 ml distilled H_2O . Add 5 ml 48% HF, stir, and centrifuge. Decant and discard supernate.
7. Transfer precipitate to 50 ml beaker with a minimum of distilled H_2O . Add 5 ml concentrated HNO_3 , 3 ml concentrated HClO_4 , and evaporate carefully to dryness without watchglass and without boiling. Cool.
8. Add 1 ml concentrated HNO_3 , 1 ml concentrated HClO_4 , place on hot plate, and cover briefly with watchglass, allowing condensate to contact entire inside surface of beaker. Remove watchglass and evaporate to dryness. Cool.
9. Add 1-2 ml 1:1 HCl, evaporate to dryness. Cool. Repeat HCl addition and evaporation. Cool.
10. (a)* Add 5 ml each 0.4 M N_2H_4 in 2 N HCl and 0.2 M KI, cover with watchglass and place on bare hot plate. Sample should be heated rapidly to just below boiling in about one minute. Swirling during the heating prevents bumping. At this point sample should be rapidly decolorizing. Place sample on asbestos mat on hot plate until completely colorless, but not to exceed a total heating period of 3 minutes. Place in cold water bath to cool.
 (b) Add 2 g solid KI, 2.5 ml 4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$, 6 ml 2 N HCl, and 2 ml distilled H_2O . Cover with watchglass, heat to 80°C for 20 minutes and cool.
11. Transfer to 60 ml separatory funnel with 3 ml 1 N HCl, add 10 ml 0.45 M TTA in benzene, and shake mechanically for 15 minutes.
12. Discard aqueous phase and wash organic layer 5 minutes each with 2-10 ml portions of 1 N HCl, followed by a one-minute wash with 10 ml distilled H_2O . Discard all aqueous fractions.
13. Strip Np from organic by shaking 15 minutes with 10 ml 8 N HCl followed by an additional 5-minute shake with 5 ml 8 N HCl.
14. Drain 8 N HCl strip solution into 15 ml beaker and evaporate to dryness, without boiling, on hot plate. Cool.
15. Add 0.5 ml each concentrated HNO_3 and concentrated HClO_4 , evaporate to dryness. Cool.
16. Add 1 ml 1:1 HCl and evaporate to dryness. Repeat HCl addition and evaporate to about 0.2 ml while covered with watchglass. Cool.

*At this point, either step 10.(a) or 10.(b) may be used. See text of report.

17. Prepare electrodeposition cell by degreasing 1/2" stainless steel discs in hot CHCl_3 , assembling cell, and adding 1 drop methyl red and 0.5 ml 12 M KOH.
18. Transfer solution from 15 ml beaker to prepared cell with 2 ml 1:1 HCl. The HCl is used to rinse the watchglass and the beaker as it drains from a 2 ml pipet. The transfer is performed so as to provide three rinses of the beaker with the acid.
19. Immediately neutralize solution in cell by dropwise addition of concentrated NH_4OH . Acidify with 1 N HCl adding 4 drops excess.
20. Electrodeposit 1 hour at 500 ma with the rotating platinum anode spaced 1 cm above the cathode disc. Quench electrolyte with 1 ml concentrated NH_4OH , before cutting current, upon completion of plating.
21. Remove cell from apparatus, rinse with distilled H_2O , and disassemble. Remove disc, rinse with distilled H_2O , and dry under heat lamp. Count disc for alpha activity.

ELECTRODEPOSITION CELL

FIG. 1

FIGURE 2

FOUR POSITION ELECTRODEPOSITION APPARATUS (CELLS IN PLACE)