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RESEARCH AND DEVELOPMENT REPORT

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FISSION PRODUCT ANALYSIS
OF URINE

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FISSION PRODUCT ANALYSIS OF URINE

by

R. C. Thorburn
Development Division
Health Instrument Divisions

May 31, 1950

HANFORD WORKS
RICHLAND, WASHINGTON

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FISSION PRODUCT ANALYSIS OF URINE

INTRODUCTION:

A chemical procedure for the analysis of the fission products, S⁸⁹, Sr⁸⁹ - Y⁹⁰ Ru¹⁰⁶ - Rh¹⁰⁶, Cs¹³⁷ and the long-lived rare earths i.e. Ce¹⁴⁴ - Pr¹⁴⁴, in urine is required for health monitoring. The present fission product analysis for urine in routine use on all samples at Hanford is known to give losses of Ru, Sr, and Cs⁽¹⁾. The Ru is lost in the muffling procedure but it was hoped that the strontium and cesium could be separated and measured.

It was desired that these elements be separated together from the bulk of the urine salts for one measurement. In addition it was desired that a procedure be obtained which would allow the use of the same sample that is used for plutonium determination. Thus it was necessary to cope with the supernate from a lanthanum fluoride precipitation and the aluminum nitrate solution remaining after a TTA extraction. The final procedure was required to be simple so that up to 500 samples per month could be processed with a minimum of manpower and equipment.

The results of this investigation are presented herein.

SUMMARY:

A method has been adapted from ion exchange studies for removal of the fission products, Cs-137, Sr-90, and the rare earths for both untreated urine samples and the supernates from the precipitation steps in the TTA procedure for plutonium.

Because of the excessive amount of eluant necessary to separate the fission products and the resulting time required to run a separation, a method was developed to remove the Sr-Y, Ce and Pr by chemical means and Cs from the raffinate of this extraction by ion exchange. It should be noted that Cs is easily separated from Pu in the separations plant, and that its presence as a contaminant in the outer areas is not as probable as the other long-lived fission products. This fact has been born out in 3 years of analyzing contaminated samples from the 200 Area by the H.I. Development Divisions.

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Detailed procedures are presented.

Experimental:

All ion columns were made from glass tubing 7 cm in diameter x 25 cm long, plugged at the bottom with a one hole rubber stopper, a glass tube and a pinch clamp control for flow rates. The resin beds were of Dowex-50 (Nalcite), 100 to 150 mesh, approximately 10 cm deep supported on 1/2" of glass wool. Feed into the column was accomplished through one liter separatory funnels. These funnels were, in turn, fed from a three gallon jug during elution. Fig. 1 is a diagram of the apparatus.

All urine samples were collected from personnel in the H.I. Development Laboratories. About 200 ml of concentrated nitric acid and varying amounts of the selected fission product were added to 1500 ml aliquots of the urine samples and these aliquots evaporated to dryness. The samples were then either wet-ashed or muffled to remove organic residues and the remaining salts dissolved in 50 ml of 2N HNO₃ with heating. This solution was used as a starting solution for the three types of analyses attempted.

It should be noted at this point, that a residue remained after digestion of these salts. No activity was observed on this insoluble residue after careful centrifugation, washing and counting.

The solubilized urine salts were then treated as dictated by experiment: (1) removal of the fission products from the raffinate of the TTA extraction with ion exchange columns (2) removal of the fission products from untreated salts with ion exchange columns and (3) removal of the fission products from the raffinate of the TTA extraction by chemical separations except in the case of Cs which was recovered with ion exchange columns.

The afore mentioned TTA procedure is used at Hanford Works in urinalysis for plutonium detection. The procedure involves the separation of plutonium from the bulk of the urine salts (prepared by evaporation with HNO₃ and a subsequent muffle at 500°C for one-half hour) with a fluoride precipitation of the Pu using

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lanthanum as a carrier. The lanthanum-plutonium fluoride precipitate is dissolved in approximately 6N $\text{Al}(\text{NO}_3)_3$ solution, followed by an extraction with 0.02M thenoyl-trifluoroacetone solution in benzene. After washing the organic phase with water, the plutonium is extracted from the TTA with a small volume of 8M HNO_3 , evaporated to dryness on a counting plate, flamed and counted to determine the amount of Pu present. As may be seen from this brief outline, Pu is separated from the urine salts and any contaminating long-lived fission products are separated at one of two places. Cs, some Sr and Ru, if present, would be removed at the LaF_3 precipitation while the rare earths and some Sr would be carried through this step and would be separated at the TTA extraction step. This leaves two distinct types of raffinate for analysis, one consisting of a hydrofluoric acid solution of the urine salts and the other consisting of an aluminum nitrate solution with traces of the urine salts.

In attempts to remove the fission products from the raffinate of the TTA extraction the urine solution under test was cooled, carriers were added and the solution treated as in the normal TTA procedure; reduction with hydroxylamine-hydrochloride, precipitation with LaF_3 , solution in aluminum nitrate and finally TTA extraction. (2) The supernate from the LaF_3 precipitation was evaporated to dryness, heated to removed NH_3 and finally treated with H_2SO_4 to remove the fluoride ion. The raffinate and washings from the TTA extraction were treated with strong caustic to remove the aluminum as soluble aluminate and the rare earths then precipitated as hydroxides. Oxalate ion was also added to precipitate any strontium that carried over as soluble strontium salts. The supernate was discarded and the resulting hydroxide plus oxalate precipitate was dissolved in a minimum amount of 2N HNO_3 , brought to dryness to destroy the oxalate ion, and the salts then dissolved in 0.25 HNO_3 . This solution was combined with the residue from the LaF_3 precipitation. The combined salt solution was diluted to approximately 100 mls. with 0.25N HNO_3 and used as the feed solution for the columns.

In attempts to remove the fission products from untreated urine salts, a solu-

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tion 0.25N in HNO_3 was made from the 2N HNO_3 solution of muffled salts. This solution was carefully centrifuged to remove the trace of insoluble material and the supernate used as feed. The precipitate was mounted for counting, and as previously mentioned, contained no activity.

In attempts to remove the fission products, Ce-Pr, and Sr-Y chemically, followed by Cs extraction with ion columns, the solution of muffled salts was put through the regular TTA procedure. The raffinate from the extraction steps was analyzed with the current procedure in use by the Hanford Bioassay Group for fission products. No attempt is made to analyze the raffinate from the LaF_3 precipitation for fission products currently and the losses noted below have been found to occur at this step. Experience with this procedure has shown good recoveries for the rare earths, approximately 40% recovery for Sr and no recovery for Cs. The supernate from the LaF_3 precipitate was analyzed for Sr. After Sr recovery it was analyzed for Cs by evaporation of the raffinate to dryness, heating to remove NH_3 , and finally solution of the salts with 0.25N HNO_3 for feed into the columns.

Two different types of analyses were used to recover Cr. The first trials were run by evaporation of the LaF_3 supernate to near dryness, and separation of the alkaline earths with fuming nitric acid followed by a $\text{SO}_4^{=}$ precipitation in acid. The strontium sulfate precipitate was washed, dried, and counted. Yields were low for this procedure. More successful attempts were run by neutralizing the LaF_3 supernate to a pH of 2, adding excess sulfate ion, heating at 90°C for 30 mins., centrifuging, washing, drying and counting the precipitate.

Column conditions and characteristics were based on previous work⁽³⁾. Flow rate was approximately 1 cc/min/cm² of resin bed. The feed solutions were all 0.25N in HNO_3 . Elutant acidity was 0.25N until all the salts were washed out, and then changed to 2N HNO_3 to remove the fission products and finally to 4N HNO_3 . It was found that 2N acid will remove Cs, Sr, and Y from the resin but that 4N HNO_3 is required to move the Ce-Pr. Sampling was continuous; every 250 ml of eluant were

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evaporated to dryness, the salts weighed and then counted.

All counting was done on the first shelf of a standard thin mica end window counter. By counting all samples with the same geometry on the same type of mount, backscatter corrections, window and air absorption corrections, and geometry corrections could be ignored in obtaining relative values. Ce was counted with its daughter; Sr measurements included the Y daughter unless specifically mentioned.

Results:

The sampling results were plotted as counts/min vs volume and as weight vs volume. In this manner the separation of the bulk of salts from the fission products could be readily discerned.

Figure II is a plot of the separation obtained on the raffinate from the TTA extraction. Three runs are plotted; one showing a Cs separation from urine salts, one showing a Sr separation and one showing the separation of Ce. It is believed that the Y^{90} band did not show during the Sr analysis because of a eight day lag in counting after the analysis.

Recovery in all these runs approached 100%.

Figure III is a plot of the Sr separation from untreated urine salts. Again good separations were obtained. The column was stopped over the weekend after 24.5 liters had gone through and then resumed. Counting was done the Wednesday following the stopover allowing considerable decay of Y^{90} . It is interesting to note the excellent separation obtained between the fission products even without the use of complexing agents.

The chemical recoveries of the fission products by the current beta process in the Bioassay laboratories has shown good recoveries for the rare earths: approximately 100% for Ce and approximately 85% for Y. Strontium recover, however, has been only around 40% and Cs recovery nil. Analysis of LaF_3 supernate for strontium by evaporation, Sr precipitation with fuming nitric acid followed by a SO_4^{2-} precipitation gave poor recoveries of about 20% of the Sr in the supernate. After neutral-

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ization with NH_4OH to a pH of 2, a SO_4^{2-} precipitation gave 100% recoveries of the Sr in the supernate. It should be noted that a four day delay was allowed after the analysis before counting. This allowed the Y^{90} to build up to transient equilibrium thus allowing a direct comparison to the counting rate of the original spike. All spike standardization was done by counting these beta emitters with 20 mg of the respective carriers. A considerable variation in counting rate due to uneven spread without carriers was found in previous work.

The Cs recovery from the Sr supernate with ion columns approached 100% and was similar in separation characteristics to that shown in Figure 2.

In summation, the ion columns gave practical separations with $100 \pm 10\%$ recoveries of the fission products and a reduction of solid content to less than 200 mgs. A rapid, simple analysis for Sr in urine salts has also been developed.

Discussion:

As may be seen by Figures 2 and 3, separation by elution only, requires a large volume of eluant which requires time. At a flow rate of 30 to 40 ml/min approximately 12 hours would be required for elution. In addition, considerable time and equipment would be required for evaporation before counting, further complicating the procedure. For these reasons, the rather rapid and simple chemical separation was developed for the complete separation of the rare earths and Sr. Ca can then be recovered from the raffinate with ion columns if desired. In three years of analyzing some 300 samples of contamination from Hanford Works only two samples showed a Cs content of over 50% of the total activity. These samples were from the R-3 area (broken waste line) and sub-surface soil samples from the geology investigations. In no case has Cs even been the only contaminant but has always been associated with either Sr^{90} or Ce^{141} .

No attempt was made to develop specific analytical determinations for each fission product. However after separations for total fission products have been made as outlined herein further separations could be easily made with standard

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fission product analyses (4).

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No attempt was made to recover Ru¹⁰⁶. Tests have shown that Ru¹⁰⁶ volatilizes from urine salts during muffling. Special samples will be required for Ru¹⁰⁶ analysis which could be adapted from the standard F.P. procedures using large equipment.

The three procedures are outlined in the appendix.

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- (3). Thorburn, R. C. Project Document HW-15742 The Separation of Radio-active Cs from Macro Quantities of Sodium and Potassium Salts. 1-27-50

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APPENDIX I

Ion column procedure for analysis of urine salts for fission products.

A. Preparation of urine for column.

1. Evaporate urine to dryness with HNO_3 and muffle salts until they are white.
2. Dissolve the muffled salts in a minimum amount of 0.25N HNO_3 .
3. Centrifuge off the small insoluble residue and wash. Plate the residue for counting and add the wash to the supernate.
4. The combined supernate and wash are the feed solution for the ion column.

B. Operation of the column.

5. The resin used is Dowex 50, particles 100-150 mesh.
6. The column is a glass tube of 65 mm diameter. It has a plug of glass wool, and a rubber stopper with an outlet tube with a screw clamp for regulating flow at the bottom. The top is fitted with some arrangement for continuous feed of dilute acid.
7. Place a column of resin 10 cm high in the glass tube. This is best done by pouring water into the column and adding the dried resin a small amount at a time. Each portion is allowed to settle before the next is added.
8. Flow rate used is 10 ml per minute for feed solution and 40 ml per minute for elution.
9. Carefully pour the feed solution into the column and let it run through.
10. Allow 17 liters of 0.25N HNO_3 to flow thru the column to wash out Na and K salts from the urine. Discard this solution.
11. Run 10 liters of 4N HNO_3 thru the column. Evaporate this solution to a small volume, transfer to a counting plate, evaporate to dryness.
12. Flame the sample and count.

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APPENDIX II

Ion column procedure for analysis of TTA raffinates for fission products.

A. Preparation of solution for column.

1. Save supernate and washings from LaF_3 precipitation step (solution A) and the $\text{Al}(\text{NO}_3)_3$ raffinate from the first TTA extraction step (solution B) for analysis.

(a). Solution A

2. Evaporate combined wash and supernate from LaF_3 precipitation to dryness. A precipitate will form during evaporation.
3. Add 10 ml conc. H_2SO_4 to dried salts and again evaporate to dryness. Salts should be heated until they are completely dry and no more fumes come off.
4. Digest dried salts with 20 ml of 0.25N HNO_3 with heat.
5. Centrifuge off the insoluble residue and wash it twice with 0.25N HNO_3 .
6. Combine washings and supernate.
7. Plate the residue and have it counted. It may contain part of the Sr.

(b). Solution B

8. Add 20 mg of Sr and Ce carrier to solution B.
9. Add conc. (at least 12 N) NaOH to $\text{Al}(\text{NO}_3)_3$ solution until $\text{Al}(\text{OH})_3$ forms and dissolves. Add 1 ml $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution.
10. Centrifuge off precipitate and wash it once with 12N NaOH and once with H_2O . Discard supernate and washings.
11. Dissolve precipitate in 5 ml 8N HNO_3 and dilute to 0.25N.
12. Combine with 0.25N solution obtained in step 6. This is the feed solution for the column.

B. Operation of column.

Follow procedure for operation of column in Procedure

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APPENDIX III

Chemical analysis of raffinates from TTA analysis for fission products with cesium by ion column separation.

1. Evaporate urine to dryness with HNO_3 and muffle until salts are white.
2. Dissolve muffled salts in 2N HNO_3 - carry out standard TTA procedure saving supernate and washing from LaF_3 precipitation for Sr and Cs analysis.
3. Neutralize supernate from step 2 with NH_4OH until it is approximately at a pH of 2.
4. Add 40 mg Sr carrier and an excess of $(\text{Na})_2\text{SO}_4$.
5. Heat solution until SrSO_4 precipitates. This can require a half hour or more. Add H_2O if volume gets too low.
6. Centrifuge and wash precipitate once with dilute Na_2SO_4 and once with H_2O . Add washings to supernate and save.
7. Transfer the precipitate to a counting plate and count for Sr.
8. Evaporate supernate to dryness to remove NH_4 salts. Disregard precipitate which forms during heating. Muffle at low heat.
9. Digest dried salts with 0.25N HNO_3 and heat.
10. Centrifuge off insoluble residue and wash it twice with 0.25 HNO_3 . Discard residue.
11. Pour combined supernate and washings thru an ion exchange resin column for Cs analysis.
12. Dissolve LaF_3 precipitate in $\text{Al}(\text{NO}_3)_3$ solution and shake with TTA solution for Pu analysis, as in standard TTA process.
13. Add concentrated NaOH (at least 12N) to $\text{Al}(\text{NO}_3)_3$ raffinate from first TTA extraction until $\text{Al}(\text{OH})_3$ has formed and dissolved; add 1 ml of saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution.
14. Centrifuge off precipitate and wash once with 12N NaOH and once with H_2O . Discard supernate and wash.

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15. Transfer the precipitate to a counting plate, dry, and count for rare
earths and strontium.

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APPENDIX IV

Resin Preparation

1. Soak required volume of Dowex 50 100-150 mesh in 4N HCl for several hours. Stir occasionally.
2. Drain acid from resin and wash in distilled H₂O to remove all traces of acid.
3. Dry resin on towel and store for future use.

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FIG. I

FEED EQUIPMENT

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FIGURE II

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FIGURE III

ELUTION OF ^{90}Sr - ^{90}Y FROM UNTREATED URINE SALTS

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