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From: R. C. Thorburn

ZIRCONIUM ANALYSIS

February 21, 1950
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INTRODUCTION:

Recent attempts to displace fixed plutonium from the body by zirconium therapy have made an analytical method for the determination of zirconium in urine salts advisable.¹ Standard chemical analytical methods^(2,3) for zirconium in rock were not adaptable to urine salts. The poor results obtained from these standard methods necessitated the development of a modified analytical procedure. The results of this work are reported herein.

SUMMARY:

Separation of zirconium from the urine salts by standard chemical methods were tried with poor results.

A clean separation was obtained by precipitating zirconium in a strong acid solution of the salts, with phosphate ion. The zirconium is then dissolved by complexing with fluoride ion and the other acid insoluble salts are removed by centrifugation. The zirconium fluoride or zirconyl fluoride complex is then destroyed by adding an excess of boron, allowing the zirconium to be reprecipitated as the phosphate. After two of these cycles, the zirconium phosphate is ignited to the pyrophosphate and weighed as such.

Acceptable yields were obtained; the method is rapid and adaptable to routine analyses.

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PROCEDURE:

All development work was done on 1500 ml samples of urine to which approximately 10 mg. of zirconium, as zirconyl nitrate, had been added. The samples were acidified with nitric acid and boiled to dryness. The salts were then muffled at 500°C for 30 minutes to remove organic residue.

The amount of zirconium added to the urine salts was determined by standardizing a solution of zirconyl nitrate with a phosphate precipitation, ignition and weighing as the pyrophosphate.

Initially, attempts were made to remove the zirconium by digesting the salts in 10% nitric acid, centrifuging the insoluble residue (which contained the zirconium precipitated by the phosphate in the urine), washing and weighing. The yields were 200 to 400% high indicating the presence of other acid insoluble salts. A phosphate precipitation on the supernate indicated that all of the zirconium had been carried down in the residue, however.

The acid insoluble precipitate was then fused with sodium peroxide and the flux digested in hot water. The insoluble residue was dissolved in HCl and heated with H_2SO_4 which was evaporated to dense white fumes, cooled, diluted with water and the zirconium precipitated with ammonium phosphate, phenyl arsonic acid or cupferron as outlined in any standard quantitative chemistry book. Yields were 10 to 20 percent low in most cases and erratic. Precipitation with mandelic acid as outlined in verbal communication with M. Lewis⁽³⁾ was also tried with low yields.

It should be noted that all of these precipitation methods gave satisfactory results when tried on standardized solutions of zirconyl salts, indicating loss during fusion. To avoid fusion of this acid insoluble residue, attempts were made to remove the zirconium from urine salts by complexing with HF. The zirconium phosphate and contaminants from the acid solution of urine salts were centrifuged, washed, slurried with 11 ml. of 1N HF, centrifuged, and the precipitate discarded. Zirconium was

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removed from the supernate in two ways, (1) precipitation as barium zirconyl fluoride⁽⁴⁾ and (2) by phosphate precipitation in acid after destruction of the zirconium fluoride complex with boron. Erratic yields from approximately 70 to 110% were obtained by the first method. Acceptable yields of 99.2% on five samples were obtained by the latter method however.

Discussion:

The details of the procedure are given below:

1. Evaporate the sample dryness.
2. Dissolve salts in 75 mls of 2N HNO₃ - heat gently if necessary.
3. Add 1 ml. of saturated tri-sodium phosphate and stir.
4. Centrifuge, wash with H₂O and discard supernate.
5. Add 1 ml 12N HF to precipitate, slurry and add 20 mls H₂O.
6. Centrifuge, wash precipitate with 5 mls. 1N HF solution.
7. Combine washings and supernate and make two normal with nitric acid.
8. Add 1 ml. saturated tri-sodium phosphate solution.
9. Add 10 saturated boric acid solution and stir.
10. Centrifuge and discard supernate.
11. Repeat steps 5 through 10.
12. Wash precipitate with H₂O.
13. Dry, ignite to red heat for 15 minutes, weigh as the pyrophosphate.

Most zirconium compounds contain hafnium to the extent of 1 to 5%. It should be noted that this procedure will carry the hafnium along as contamination.

The Method outlined above is rapid, adaptable to routine use and requires a minimum amount of equipment. Results on unknown urine samples have been relatively confirmed by P. Anderson at the Technical Division's spectrographic lab. A series of standards were prepared with 1 mg. of Zr/20 gms. of salts, 2 mg. 20 gms. of salts, 5 mg/20 gms of salts, 10 mg/20 gms of salts and 20 mg/20 gms of salts. Plates from these standards were compared to plates from two unknown samples. The relative order

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of magnitude obtained in these two samples were similar to the results obtained by the chemical method.

It is possible that this method may be adapted to other types of samples.

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REFERENCES

1. Schubert, J. Treatment of Pu Poisoning by Metal Displacement. LMDC-595.
December, 1946.
2. Furman, Ed N. E. Scotts' Standard Methods of Chemical Analysis.
3. Schmidt, H. R. Analytical Research Group Report - Redox. HM-13539.
December 29, 1949. September and October, 1949.
4. Hume, D. N., Ballou, N. E., Glendenin, L. E. A Manual of the Radiochemical Determination of Fission Product Activities. OR-2815.

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