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BIOLOGY SEMINAR

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METHODS OF ASSAYING FOR PLUTONIUM IN BIOLOGICAL MATERIALS

by A. C. Case

Biology Division

Health Instrument Divisions

General Electric Company

Hanford Works

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I. INTRODUCTION

Since plutonium is manufactured at the Hanford Works, a study of its effect on biological materials is important. To determine the amount of plutonium deposited in a biological sample, it is necessary to have an accurate method for extracting plutonium from these samples. Some of the different methods for plutonium assay are reviewed and given in this paper.

There are two main isotopes of plutonium, one with an atomic weight of 238 and the other with an atomic weight of 239. One μg of Pu^{239} yields 1.4×10^5 d/m of alpha particles with energy of 5.15 MEV. Plutonium may be found in several valence states. These are 0, $+2$, $+3$, $+4$, $+5$, and $+6$. The 0 state is the metallic form. The $+2$ state is not found in solutions. The black tarnish on the free metal is thought to be PuO . Plutonium in the $+3$ state is easily oxidized to higher valences by air or other oxidants which in high concentrations is a blue-violet color when in solution. The $+4$ state is the common one found in aqueous solutions. Plutonium in the $+5$ state is unstable and is produced by controlled electrolytic or chemical reduction of the $+6$ state. The highest valence state found is $+6$. Plutonium solutions should be kept acid since it tends to adsorb out on the glass containers in neutral or alkaline media.

II. METHODS OF ASSAY

A. Materials of High Specific Activity

For these samples, it is often satisfactory to put the sample into solution in acid, and dry an aliquot on a stainless steel plate. The amount of solid left on the plate must be kept at a minimum to reduce the self absorption.

B. Materials of Low Specific Activity

These samples are ashed first to remove the organic matter. This can be done by the dry method (muffling), the wet method (with fuming HNO_3 and H_2O_2), or a combination of the two. A further concentration of the plutonium from the remaining inorganic salts is desired before counting. The following are some of these concentrating methods.

1. Cupferron-chloroform Method (1)

Cupferron and chloroform have been used on plutonium spiked urine samples. This is done by mixing cupferron with the urine, followed by a chloroform extraction. The chloroform containing plutonium was evaporated on a plate for counting. The percent recovery was quite variable and not too high. Also the interface between the CHCl_3 and the urine was ill-defined, making good separation difficult.

2. Resins Method (2,3)

Various resins have been used to try to concentrate plutonium from urine samples. Both column and batch extractions have been tried. Often a gelatinous precipitate plugged the column.

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The batch method is to stir the urine with the resin, decant the liquid, and wash the resin into a funnel. The plutonium is removed with 6 N HCl. Water spikes give fair results, but urine samples give low and non-reproducible percentages, even when identical conditions are met.

3. Lanthanum Fluoride Method (2)

Several "carriers" may be used which, when they are precipitated, will carry along the plutonium. One such method uses LaF_3 . The process is to add the lanthanum ion, and precipitate with HF. Then spread, dry, and count the precipitate. Recovery is quite good for small samples of at least moderate activity. Calcium also forms a precipitate under these conditions and hinders the determination in bone samples.

4. Bismuth Phosphate Method (1,2)

An extension of the above method is to precipitate bismuth carrier with phosphoric acid followed by dissolving the precipitate in 2 N HCl and performing a lanthanum fluoride procedure on the solution. Closely controlled conditions give recoveries of about 80% for small urine samples of high activity.

5. Zirconium Phosphate Method (1,2,4,5)

It is also possible to precipitate zirconium carrier with phosphoric acid, dissolve, and follow with a lanthanum fluoride procedure. This is often done on bone samples where there is a high calcium content. The method gives about 80% recovery on 25cc spiked urine samples.

6. Hexone Method (6)

Hexone (isobutylmethyl ketone) can be used to concentrate plutonium. A preliminary precipitation with lanthanum carrier and HF is first performed. The precipitate is dissolved and the plutonium extracted into a hexone layer. Re-extraction into a water layer, followed by another lanthanum fluoride precipitation finishes the procedure. 75% of the original activity goes into the hexone layer with one extraction.

7. TTA Method (7,8,9,10)

The TTA (thenoyl-trifluoroacetone) method is the one used here at Hanford for the analysis of urine samples. TTA is one of several trifluorinated compounds which complex plutonium in the $+4$ valence, making it extractable into a non-polar solvent such as benzene. The procedure is first to carry out a lanthanum fluoride precipitation. This is dissolved in an $\text{Al}(\text{NO}_3)_3$ solution, and extracted with a benzene solution of TTA. This may be evaporated directly to stainless steel plates, or a re-extraction into 8 N HNO_3 maybe performed, and the HNO_3 evaporated. Advantages of this method are the negligible amounts of matter left on the plates, and the removal of most of the alpha contamination present in lanthanum. Results on water spikes and small samples of urine, feces, tissue, etc. are 90-99% recovery.

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III. SUMMARY

The choice of a method to use depends upon the conditions and facilities available. Both the cupferron and resins methods prove unsatisfactory, especially for urine samples. The LaF_3 method is short and quite satisfactory for small samples of low calcium content with fairly high specific activity. The bismuth phosphate and zirconium phosphate methods try to remove the difficulties encountered with samples of high calcium content. These procedures are longer and demand more exacting conditions. The hexone method is also long, but not too difficult. The TTA process has an advantage that a very small amount of matter is left on the plates. It is also fairly easy to carry out.

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