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PAPERS PRESENTED AT THE EIGHTH ANNUAL MEETING
ON BIO-ASSAY AND ANALYTICAL CHEMISTRY

October 18 and 19, 1962

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INTRODUCTION

The Eighth Annual Bio-Assay and Analytical Chemistry Conference was held October 18 and 19, 1962 in Augusta, Georgia. The meeting was sponsored by the Health Physics Section of the Savannah River Plant. Similar conferences, sponsored by other organizations, were held each year since 1955. The proceedings of previous meetings were issued as reports NCL0-595, WASH-736, WASH-1023, TID-7591, TID-7616 and ANL-6637. No proceedings were issued for the meeting held in 1957.

The primary purpose of these conferences is to provide an opportunity for people working in the field of bio-assay or health radiochemistry to exchange information and discuss problems of mutual interest.
The determination of small amounts of radiocesium in natural materials by gamma-ray spectrometry is often complicated by the presence of fission products and other neutron-induced activities, as well as natural potassium. When these interfering activities reach sufficiently high levels, the cesium must be separated chemically for accurate counting. Cesium forms an insoluble hexachlorostannate in hydrochloric acid solution that can be used as the basis for such a separation. In this procedure decontamination from fission products and other interfering activities, except potassium, is accomplished by ferric hydroxide scavenging precipitations and by precipitation of the radiocesium (with cesium carrier) as the hexachlorostannate. Separation from the bulk of the potassium is obtained by precipitation of potassium chloride from hydrochloric acid-ethyl alcohol solution. Separation from the remaining potassium is accomplished by precipitation of cesium hexachlorostannate since the corresponding potassium salt is considerably more soluble.

The final cesium hexachlorostannate precipitate may be counted by any suitable method. The procedure has been used to determine radiocesium in water, precipitation, milk, soil, vegetation, air particulates, and urine.
INTRODUCTION

Cesium forms a large number of slightly soluble compounds with complex anions, and many of these compounds have been used for gravimetric and radiochemical separations and determinations. Among the complex halogen compounds, the chloroplatinate (1,2,3) has received the most use, and radiochemical methods using cesium bismuth iodide (3,4) have been reported. The first use of cesium hexachlorostannate (Cs₂SnCl₆) for a quantitative cesium determination was reported in 1925 (5) and a procedure based on this compound is given in the first edition of Applied Inorganic Analysis (6), although it is omitted in the revised 1953 edition (1). A radiochemical chlorostannate procedure was reported by Lyon (7), but the work described here was begun before this publication appeared, and the procedure by Lyon does not provide for potassium removal and no data on decontamination are given.

In the analysis of materials containing macroscopic amounts of potassium and very small amounts of radiocesium activity, the most important and critical portion of any procedure is the potassium-cesium separation. In this procedure the potassium is removed by precipitation of its chloride from alcohol-hydrochloric acid solution prior to the precipitation of cesium hexachlorostannate. Thus, the maximum amount of potassium that can appear with the cesium is determined by the solubility of potassium chloride in the solution used. In fact, the success of the procedure is dependent on the relative solubilities of chloride salts, particularly the alkali metal chlorides.
ANALYTICAL PROCEDURE

1. To a solution of the sample add 20 mg. of cesium carrier (Note 1) and evaporate the solution to dryness. Transfer the residue to a 100 ml. centrifuge tube using 0.1N nitric acid as the wash solution.

2. Heat the solution to boiling, add 5 mg. of Fe(II1) carrier, stir well, and neutralize by adding concentrated ammonium hydroxide dropwise until the precipitate coagulates. Avoid a large excess of ammonium hydroxide. Centrifuge and decant the filtrate into a clean 100 ml. centrifuge tube. Wash the precipitate well with 10 ml. of water containing one drop of concentrated ammonium hydroxide. Centrifuge, add the wash solution to the original supernatant and discard the precipitate.

3. Repeat Step 2, except omit the addition of ammonium hydroxide.

4. Evaporate the solution to dryness. Add 5 ml. of 6N hydrochloric acid, evaporate to dryness again, and allow to cool. Add 10 ml. of alcohol-hydrochloric acid reagent (Note 2) and stir the solution for 15 minutes with a motor driven stirring rod. Centrifuge and decant the supernatant into a clean 100 ml. centrifuge tube. Wash the precipitate with 10 ml. of alcohol-hydrochloric acid solution, centrifuge, and add the wash solution to the original supernatant.

5. To the supernatant add 10 ml. of stannic chloride solution (Note 3), stir, and allow to stand for 15 minutes. Centrifuge, discard the supernatant, and wash the precipitate of cesium hexachlorostannate with 10 ml. of absolute ethyl alcohol. Centrifuge and discard the wash solution.
6. Dissolve the precipitate in 10 ml. of 2N nitric acid, warming if necessary to obtain complete dissolution. Evaporate the solution to a few tenths of a milliliter, and reprecipitate the chlorostannate by adding 10 ml. of alcohol-hydrochloric acid solution. Allow the precipitate to stand for 15 minutes. Centrifuge, discard the supernatant, and wash the precipitate with 10 ml. of absolute ethyl alcohol. Centrifuge and discard the wash solution.

7. Repeat Step 6.

8. Filter the precipitate on a previously weighed filter paper, using absolute ethyl alcohol to transfer the precipitate. Dry the paper and precipitate in an oven at 110°C for 10 minutes, cool, weigh to obtain the cesium recovery, and mount the paper for radioactivity measurements. Count the activity in any suitable manner. Before use, wash the filter paper with approximately the same volume of absolute ethyl alcohol used to transfer the precipitate, dry the paper at 110°C, and weigh.

NOTES

(1) The cesium carrier is added as a solution containing approximately 10 mg. of cesium ion per milliliter. It is prepared by dissolving 12.6 g. of cesium chloride in water and diluting to one liter with distilled water. The carrier solution is standardized as follows. Pipet 5 ml. of carrier solution into a 50 ml. beaker, and evaporate to a few tenths of a milliliter. Add 20 ml. of solution containing 0.1M Sn(IV) in alcohol-hydrochloric acid. This solution is prepared by diluting 2 ml. of the stannic
chloride solution described in Note 3 to 20 ml. with the alcohol-hydrochloric acid solution given in Note 2. Allow the cesium hexachlorostannate precipitate to stand for 15 minutes, and filter quantitatively on a fine-porosity sintered glass crucible, using absolute ethyl alcohol to transfer and wash the precipitate. Prior to the filtration, wash the crucible with three 20 ml. portions of distilled water followed by five 20 ml. portions of absolute ethyl alcohol. Dry the crucible at $110^\circ$ C. for 10 minutes, cool, and weigh. Repeat the drying and weighing until constant weight is obtained. Dry the crucible containing the precipitate to constant weight in a similar manner.

(2) The alcohol-hydrochloric acid reagent is prepared by mixing two volumes of absolute ethyl alcohol with one volume of reagent-grade concentrated hydrochloric acid.

(3) The stannic chloride solution is prepared by dissolving 105 g. of stannic chloride pentahydrate in 50 ml. of concentrated hydrochloric acid and adding 200 ml. of absolute ethyl alcohol. The final volume of this solution is 300 ml. and the stannic ion concentration is one molar.
DISCUSSION

The solution is first evaporated to dryness to remove any excess volatile acids, and in this way the amount of ammonium hydroxide required to neutralize the solution in Step 2 is kept to a minimum. If phosphate and alkaline earths are present, they should be completely precipitated, and the filtrate can be tested for complete precipitation. Two ferric hydroxide precipitations are used initially to obtain some decontamination. Any tin, antimony, and tellurium fission products in the sample may precipitate with the cesium chlorostannate and are removed by these scavenging precipitations along with many other fission products. Antimony and tellurium form insoluble compounds with cesium and chloride ion under the same conditions as tin. The evaporation in the presence of hydrochloric acid in Step 4 serves to destroy the ammonium and nitrate ions, and can be repeated if large amounts of ammonium ion are inadvertently added. The evaporation must be done carefully. If the solids are baked, it is difficult to redissolve the cesium completely when large amounts of solids are present. If too much liquid remains, the potassium is incompletely removed in the next step and some will appear with the cesium chlorostannate. Best results are obtained if the evaporation is stopped when the solids are barely moist. The addition of hydrochloric acid prior to evaporation also aids in building up the chloride ion concentration if the evaporation is not carried far enough. The use of a minimum amount of ammonium hydroxide and the removal of ammonium ion at this stage are very important since ammonium ion is not completely separated later in the procedure and will precipitate with the cesium as ammonium chlorostannate.
Step 4 serves primarily to remove potassium as the chloride, but also removes the sodium and part of the rubidium and ammonium if present in amounts exceeding their solubilities. The solubilities of potassium and sodium chlorides in the alcohol-hydrochloric acid mixture are such that their chlorostannates will not precipitate from their saturated solutions in this reagent. In fact, if potassium chloride is added to the solution from which cesium chlorostannate is precipitated, potassium chloride precipitates before potassium chlorostannate. However, as will be seen, fractional milligram amounts of potassium are carried by the cesium and contribute a blank to the counting rate, but the chemical yield is not appreciably affected. Three cesium chlorostannate precipitations complete the procedure.

The chlorostannate precipitate is very finely divided, and if it is prepared for counting by filtering onto paper in a chimney-funnel arrangement in the usual way, the precipitate forms a very smooth and uniform pad very suitable for beta counting. The chimney and funnel must fit very tightly to prevent loss of precipitate (up to 15% can be lost in this way), and an O-ring is used between the chimney and funnel to minimize this loss. The precipitate is not completely retained by Whatman 42 paper unless the initial portion of the filtrate is poured through the paper again. Several percent may be lost in this way.

Cesium chlorostannate is quite insoluble in ethyl alcohol, ethyl ether, and alcohol-hydrochloric acid mixtures. It is only slightly soluble in concentrated hydrochloric acid, and the solution chosen for the precipitation, 2:1 (by volume) ethyl alcohol-hydrochloric acid, was the same as that used in the original paper on this subject (5). The optimum ratio of alcohol to
hydrochloric acid was not investigated, but the 2:1 mixture appears quite satisfactory. The alcohol is necessary to keep the potassium chloride solubility low in the chloride precipitation step, but is not essential for the cesium chlorostannate precipitation. The amount of stannic ion necessary for complete cesium precipitation can be varied within wide limits, from the minimum amount required by the stoichiometry of the reaction up to 3 molar. Above 3 molar the cesium precipitation is incomplete, probably because of the large amount of water added as water of hydration of stannic chloride. From 6M Sn(IV) about 70% of the cesium is precipitated. In the cesium chlorostannate precipitation step of the procedure the final Sn(IV) concentration is 0.33M. Cesium chlorostannate can be dissolved in tartaric acid (5), but reprecipitation is difficult. It is moderately soluble in water (perhaps stannic oxide precipitates), but 20 mg. of cesium (as \( \text{Cs}_2\text{SnCl}_6 \)) cannot be completely dissolved in 10 ml. of water, even on boiling. However, the precipitate is completely soluble in moderate amounts of nitric acid, 1M or greater, and this is convenient and useful since any remaining ammonium ion is removed when the nitric acid is evaporated. The nitric acid solution can be evaporated to dryness, and the cesium completely precipitated as the chlorostannate by the addition of the alcohol-hydrochloric acid reagent alone. This procedure can be repeated as often as required. Since additional Sn(IV) is not needed, the problem of washing large amounts of Sn(IV) from the final precipitate to obtain an accurate weight does not arise. The cesium carrier was standardized by precipitation from 0.1 Sn(IV) to minimize this problem. Under the conditions used, 20 mg. of cesium carrier in 20 ml. of solution, the precipitate forms slowly, 15 minutes being required for complete precipitation.
The effectiveness of the chloride precipitation in separating other alkali metals can be seen from Table I, which gives the solubilities of the alkali metal chlorides in several hydrochloric acid solutions. The measurements were made at room temperature unless otherwise indicated. In the first column are the solubilities in the 2:1 mixture adopted for the procedure. Lithium chloride is quite soluble in these systems, but since lithium chlorostannate cannot be precipitated from alcohol-hydrochloric acid solutions, it presents no problem. The solubilities of sodium and potassium chlorides are about 0.3 mg./ml. at room temperature in the 2:1 mixture. The decrease in solubility at 0°C, or in the 2:1 mixture saturated with hydrogen chloride gas, is not sufficiently great to warrant the use of these conditions. Rubidium is quite soluble in the alcohol-hydrochloric acid mixture, and since rubidium chlorostannate will precipitate from a saturated solution of rubidium chloride in 2:1 alcohol-hydrochloric acid at room temperature or 0°C, separation from macroscopic amounts of rubidium cannot be obtained, and separation from trace rubidium is poor. The solubility of rubidium chloride in ethyl alcohol saturated with hydrogen chloride gas is about the same as that of sodium or potassium chloride in 2:1 ethyl alcohol-hydrochloric acid, and it might be thought that rubidium separation in the former solution would be equal to the potassium or sodium separation in the latter solution. However, the improvement is not pronounced since rubidium chlorostannate is not very soluble, and will partially precipitate when Sn(IV) is added to a saturated solution of rubidium chloride in ethyl alcohol saturated with hydrogen chloride gas. With Rb\(^{86}\) tracer, the decontamination factor for rubidium using the 2:1 ethyl alcohol-hydrochloric acid solution is 3 at room temperature and 6 at 0°C. Using the ethyl alcohol saturated with hydrogen chloride gas, the rubidium decontamination factor is 8.6 at room temperature.
### Table I

**Solubilities of Alkali Metal Chlorides in Hydrochloric Acid Mixtures**

(milligrams per milliliter)

<table>
<thead>
<tr>
<th></th>
<th>EtOH-con. HCl (2:1 by volume)</th>
<th>EtOH-con. HCl (2:1) Sat. HCl</th>
<th>EtOH-con. HCl Sat. HCl</th>
<th>EtOH - Sat. HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>&gt;20</td>
<td>19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.29 (R.T.) 4 &lt; 20</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KCl</td>
<td>0.32 (R.T.) 4 &lt; 20</td>
<td>0.24</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>RbCl</td>
<td>3.4 (R.T.) 4 &gt; 20</td>
<td>-</td>
<td>-</td>
<td>0.30</td>
</tr>
<tr>
<td>CsCl</td>
<td>&gt;20 (R.T.) 4 &gt; 20</td>
<td>18</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>-</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1. A mixture of 2 volumes of absolute ethyl alcohol to one volume of concentrated hydrochloric acid and saturated with hydrogen chloride gas.
2. Concentrated hydrochloric acid saturated with hydrogen chloride gas.
3. Absolute ethyl alcohol saturated with hydrogen chloride gas.
4. Room temperature.
when a weighable amount of potassium chloride is also present, and 12.3 when rubidium carrier is present. It is possible that some other chloride system could be found that would give a good rubidium-cesium separation, but this does not appear necessary for fission product analysis since the initial ratio of Cs$^{137}$ to 18.7 day Rb$^{86}$ (the longest-lived rubidium fission product) is about 228 with thermal neutrons on U$^{235}$ in spite of the high specific activity of Rb$^{86}$ compared to Cs$^{137}$. This fortunate occurrence is the result of the fact that Rb$^{86}$ is a shielded nuclide, making its fission yield very low, $2.9 \times 10^{-5}\%$(8).

Ammonium chloride is fairly soluble in alcohol-hydrochloric acid mixtures, and ammonium chlorostannate is fairly insoluble. Ammonium ion cannot be separated by the precipitation reactions used, and must be destroyed by oxidation as mentioned earlier. Calcium and magnesium chlorides are soluble, but do not precipitate with stannic chloride.

The decontamination factors for a number of commonly encountered activities are given in Table II. Except for potassium, the decontamination factors were determined with tracer concentrations of these isotopes. If better decontamination is desired, additional precipitations can be used. In particular, the ruthenium decontamination could stand some improvement, and a volatilization step could be incorporated into the procedure in place of additional cesium reprecipitations. Where a greater-than figure is given, it was not felt necessary or desirable to use sufficiently large amounts of the tracer to obtain a definite value. Although they are not particularly common, antimony, tin, and tellurium were tested since they form insoluble compounds with cesium and chloride in concentrated chloride solutions. Iodine-131 decontamination was measured since it was present in the tellurium tracer. The alpha emitters,
## TABLE II

SEPARATION OF OTHER ACTIVITIES BY CESIUM CHLOROSTANNATE PROCEDURE

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Decontamination Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$^{90}$</td>
<td>$3 \times 10^5$</td>
</tr>
<tr>
<td>Ru-Rh$^{106}$</td>
<td>$1.7 \times 10^3$</td>
</tr>
<tr>
<td>Ce$^{144}$</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>Co$^{60}$</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>Fe$^{59}$</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>Zr-Nb$^{95}$</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>Sb*</td>
<td>$5 \times 10^5$</td>
</tr>
<tr>
<td>Sn*</td>
<td>$6 \times 10^4$</td>
</tr>
<tr>
<td>Te*</td>
<td>$&gt; 10^5$</td>
</tr>
<tr>
<td>I$^{131}$</td>
<td>$\sim 10^5$</td>
</tr>
<tr>
<td>U$^{233}$</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>Pu$^{239}$</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>Rb$^{86}$</td>
<td>$3 \ (R.T.)$</td>
</tr>
<tr>
<td></td>
<td>$6 \ (0^\circ C.)$</td>
</tr>
<tr>
<td>K(natural)</td>
<td>$\equiv 1 \ dpm \ Cs^{137}$</td>
</tr>
</tbody>
</table>

*Mixture of isotopes.*
$^{233}\text{U}$ and $^{239}\text{Pu}$, were tested since the beta counters used are sensitive to alpha particles and some of the samples for which this procedure is used contain considerably more uranium and plutonium activity than cesium activity. Separation from rubidium has been discussed, and it is obvious that the procedure cannot be used in the presence of weighable amounts of rubidium. The decontamination from $^{40}\text{K}$ was measured by using sufficient potassium chloride to obtain a chloride precipitate with the alcohol-hydrochloric acid reagent. The beta activity in the final cesium precipitate was equivalent to 0.5 dpm of $^{137}\text{Cs}$

$^{137}\text{Cs}$. This corresponds to about 0.3 mg. of potassium, and constitutes a blank in the counting rate (of 0.5 dpm) and makes the yield about 3% too high if the potassium is carried by the cesium chlorostannate as potassium chlorostannate or 1% if carried as potassium chloride. The blank correction must, of course, be made, but the differences between the chemical and radiochemical yields, and the direction of these differences, are the same in the absence or presence of large amounts of potassium. Thus, the accuracy in determining the chemical and radiochemical yields is insufficient to detect an error in the chemical yield of cesium due to the presence of potassium.

In two of the precipitations, cesium is supposed to remain in solution while other substances are precipitated. This is not the most desirable way to obtain efficient separations because of the possibility of loss of cesium on the precipitate to be discarded. Such losses do occur, and are important unless care is taken to minimize them. The chloride precipitation causes the most serious problems. When 5 g. of potassium chloride is precipitated with 10 ml. of alcohol-hydrochloric acid solution in the presence of 20 mg. of cesium, about 25% of the cesium is carried. Simple mild stirring with alcohol-
hydrochloric acid wash solution does not remove much of the cesium from the precipitate. However, if the precipitate and the original solution are stirred vigorously with a motor driven stirrer for 15 minutes, the cesium carrying is reduced to 15%. Additional stirring time gives only a few percent improvement. When the supernatant is removed after this treatment, the additional washes are effective when the precipitate is stirred by hand for a minute or two. Thus, washing once with 10 ml. of alcohol-hydrochloric acid solution reduces the cesium carrying from 15% to 6%. After a second wash 2% remains and after a third wash, 1.6% remains. These results indicate that the cesium taken up by the potassium chloride crystals is more readily available to the solution once the crystals are reduced in size by vigorous stirring. The cesium loss in the first ferric hydroxide precipitate is 7% when the analysis is performed on 2 liters of river water, containing 100-200 milligrams of other metals that also precipitate, and vigorous stirring has no effect. One wash reduces the loss to 3.5%. If only the added iron precipitates, less than 1% of the cesium is carried. The losses in precipitating cesium are small, less than 1% and usually only 0.5%. The overall yield of the procedure is about 85% and the operator time required is about 4 hours for a batch of four. The elapsed time is greater because of the evaporations. The method has been used on surface water (2 liters), milk (1 liter), urine (500 ml.), and solutions of soil. Chemical and radiochemical yields have been the same within ± 4%, and differences between them occur at random in both directions. This correspondence between chemical and radiochemical yields has been used as the criterion for successful application of the procedure to a given type of material.

This procedure will probably be difficult to use on sea water because of the very large amount of chloride precipitate that will be obtained (increasing...
the cesium loss) and because of the difficulty in removing sufficient water from the filtrate after the hydroxide precipitations to keep the sodium and potassium solubility low. A better approach with samples containing very large amounts of solids would be to precipitate cesium chlorostannate first to separate as much of these salts as possible. After this step, it would be necessary to remove or reduce the Sn(IV) to continue with the procedure as outlined. This can certainly be done without much difficulty, but lengthens and complicates the procedure and is not necessary for the types of samples that have been used.

Cesium bromostannate has also been investigated, but the rubidium-cesium separation is not improved when the bromide system is used in place of the chloride system. Rubidium bromostannate precipitates from a saturated solution of rubidium bromide in 2:1 (by volume) ethyl alcohol-hydrobromic acid. In addition, the relative solubilities of cesium and potassium bromides are not as favorable for a cesium-potassium separation as the chlorides, and this system was abandoned after preliminary experiments.

The chlorostannate procedure for cesium is simple, does not use any expensive or dangerous reagents, produces a cesium precipitate with physical properties well suited for accurate beta counting, and gives good decontamination from a large number of activities. Gamma counting, of course, can also be used. Its principal drawback as a general radiochemical method for cesium is the inadequate separation from rubidium, and the difficulties encountered when large amounts of cations are present in the sample. The latter problem can be overcome by a preliminary cesium chlorostannate precipitation as mentioned above.
REFERENCES


THE RADIOCHEMICAL DETERMINATION OF Cs\textsuperscript{137} IN COMPLEX MATRICES

W. R. Collins, Jr.
Health and Safety Laboratory
U. S. AEC, New York

A radiochemical method for the determination of cesium-137 in 100 gram soil samples is presented. The radiocesium and added cesium carrier are equilibrated by fusion with sodium carbonate and separated from bulk constituents in soil by leaching the melt with hot water. Cesium is separated from sodium by batch extraction onto ammonium phosphomolybdate and separated from potassium and rubidium by reprecipitation of the phosphomolybdate derivative in the presence of excess ammonium ions. Molybdenum is removed by precipitation as calcium molybdate and ammonia by volatization from acid solution. Cesium is finally collected as the chloroplatinate and assayed gravimetrically and radiometrically.

Adaptations of the basic soil technique to other matrices are discussed. Preliminary soil, food and bone data are presented.
INTRODUCTION

The determination of radiocesium in environmental samples is complicated by the presence of large quantities of inert substances and a large number of interfering natural and artificial radioactivities. In special cases, where activity levels have been sufficiently high, direct gamma ray spectroscopy has been utilized and many useful data have been obtained for rainwater, foodstuffs, biological materials and, in some instances, soils(1,2). The final practical approach, however, to routine analysis of low-level materials is through radiochemical or some combination of chemical and spectroscopic techniques.

The primary chemical interference in soils and other complex matrices are bulk quantities of silicon, calcium, iron, aluminum, and macro concentrations of the alkali metals. Isolation of cesium from these materials by classical and conventional ion-exchange methods is involved and often requires long analysis times and large sample volumes. For this reason great emphasis has been placed during recent years on the refinement of techniques employing the highly specific exchange capacities of the "alkali" salts of some of the 12-heteropoly acids. Hara(3), Krtić(4), and Caron and Sugihara(5), for example, have reported separations of cesium with thallium phosphomolybdate, ammonium phosphotungstate, and thallium phosphotungstate, respectively. Mizzi(6) and Schroeder and Cherry(7) have used phosphotungstic and silicotungstic acids. Wilding(8) and Kahn, et al.,(9) have analyzed reactor wastes and river waters with ammonium phosphomolybdate. These and other techniques, which have resulted in the successful analysis of samples as large as 200 liters of sea water and as complex as fresh mixed fission products, have been summarized by Reilley(10), Finston and Kinsley(11),

- 22 -
and Kusaka and Meinke\textsuperscript{(12)}.  

This paper reports investigations made at the Health and Safety Laboratory, of the determination of cesium in soil, vegetation, milk, and bone samples solutions with ammonium phosphomolybdate. Batch extraction techniques have been applied to facilitate handling of samples ranging in volume from 1 to 4 liters. Separation and purification methods which are readily integrated with accepted alkaline fusion and acid dissolution schemes for radiostrontium\textsuperscript{(13)} have been stressed.

The radiocesium in soils and ashed samples is equilibrated with added cesium carrier by fusion with sodium carbonate or dissolution in hydrochloric acid. Bulk constituents, including the alkaline earths and iron are removed either by leaching the fusion melt with hot water, in the case of soils or vegetation ash, or by scavenging the hydrochloric acid sample solution by precipitation of calcium phosphate. Cesium is then absorbed onto ammonium phosphomolybdate and separated from potassium and rubidium by reprecipitation of the phosphomolybdate derivate in the presence of excess ammonium ion. An alternate method involves the absorption on and the preferential elution from a cation exchange resin, Bio-Rex 40 (50-100 mesh). Cesium is finally collected as the chloroplatinate or the tetraphenylborate and assayed gravimetrically and radiometrically.

**EXPERIMENTAL**

The proposed procedures for the determination of cesium in soils, vegetation, bone, and milk ash samples are illustrated in Figure 1. Selections of the individual steps were based on preliminary investigations in this laboratory and reported efficiencies in the literature. The availa-
FIGURE 1: ANALYTICAL FLOW CHART

Na$_2$CO$_3$ Fusion; H$_2$O Leach

Collection of K, Rb, Cs with APM

γ Spectrometric Assay

Removal of K and Rb Volatilization of NH$_3$ CaMoO$_4$ Scavenge

Gravimetric Det'N as Cs$_2$PtCl$_6$

β Activity Assay

Acid Dissolution; Ca$_3$(PO$_4$)$_2$ Scavenge

Selective Absorption and elution of Cs from Bio-Rex 40

Gravimetric Det'N as Cs (TPB)
bility of cesium in the alkali fusion to a water leach has been used previously by Welford, et al., (14) and the calcium phosphate scavenging of milk and bone sample solutions is already standard at the Health and Safety Laboratory (13). The batch techniques for the ammonium phosphomolybdate extraction have been used in the work of Wilding (8). The removal of K and Rb from the phosphomolybdate fraction by reprecipitation in the presence of excess ammonium ion is consistent with the findings of Smit, et al., (15) on the stability constants of the alkali phosphomolybdate derivatives. The use of strongly acidic sulfonated phenolic resins, such as Bio-Rex 40, in alkali separations is well known. Application of the cesium tetraphenylborate determination have been reported by Handley and Burros (16).

The preliminary evaluations were performed with samples simulated from stock solutions and cesium-137 and rubidium-86 solutions obtained from Oak Ridge National Laboratory. Measurements were made gravimetrically and radiometrically using standard beta activity counting equipment (13,17) and a Nuclear Data 256 channel analyzer coupled to a 3 x 4 inch sodium (thallium) iodide gamma scintillator. The overall procedures and some of the individual steps were evaluated by processing the experimental samples listed in Table 1.

Reagents and Apparatus

1. Cesium carrier solution - 30 mg Cs⁺/ml. Dissolve 38.0 grams of CsCl in H₂O. Dilute to 1 liter with H₂O. Standardize the cesium concentration by precipitation with chloroplatinic acid.

2. Ammonium phosphomolybdate - (NH₄)₃[PMO₁₂O₄₀]. Dissolve 100 grams of molybdic acid (85% MoO₃) in a mixture of 240 ml H₂O and 140 ml NH₄OH.
<table>
<thead>
<tr>
<th>Sample Type and Number</th>
<th>Collection Site and Date</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil-614</td>
<td>Salisbury, Southern Rhodesia, 1960</td>
<td>Low normal Cs content</td>
</tr>
<tr>
<td>Soil-60424</td>
<td>Kingston, Rhode Island, 1960</td>
<td>High normal Cs content</td>
</tr>
<tr>
<td>Soil-601074</td>
<td>Ft. Amador, Panama, 1960</td>
<td>High normal Cs content</td>
</tr>
<tr>
<td>Soil-C7164</td>
<td>Decatur, Georgia, 1941</td>
<td>Fission product blank</td>
</tr>
<tr>
<td>Soil-C3188</td>
<td>Kalkaska, Michigan, 1937</td>
<td>Fission product blank</td>
</tr>
<tr>
<td>Soil-1D</td>
<td>Nevada Test Site, 1957</td>
<td>High Si content; Old fission products from Diablo, Shasta, and Whitney Tests, 1957</td>
</tr>
<tr>
<td>Soil-1E</td>
<td>Nevada Test Site, 1962</td>
<td>High Si and Fe content; Fresh fission products from Eel Test, 1962</td>
</tr>
<tr>
<td>Soil-10784</td>
<td>Raleigh, North Carolina, 1958</td>
<td>High Fe and Ca content; 257 d/m Cs$^{137}$/kg</td>
</tr>
<tr>
<td>Soil-10783</td>
<td>Chicago, Illinois, 1958</td>
<td>Low Ca and high Si content; 386 d/m Cs$^{137}$/kg</td>
</tr>
<tr>
<td>Vegetation-13973</td>
<td>Bucks Co., Pennsylvania, 1959</td>
<td>Oat ash</td>
</tr>
<tr>
<td>Bone-B0126</td>
<td>New York, New York, 1960</td>
<td>Beef soup bone composite</td>
</tr>
<tr>
<td>Milk-7604</td>
<td>Perry, New York, 1959</td>
<td>Composited powdered milk</td>
</tr>
</tbody>
</table>
When solution is complete, filter and add 60 ml of HNO₃. Mix 400 ml of HNO₃ and 960 ml of H₂O. Allow both solutions to cool to room temperature. With constant stirring add the ammonium molybdate solution to the nitric acid solution. Allow to stand for 24 hours. Filter through a #42 Whatman filter paper. Discard the insoluble material.

Collect the filtrate in a 3 liter beaker and heat to 50-55°C. Remove from heating unit. It is important that the solution is not heated above 55°C in order to avoid the contamination of the precipitate with molybdic anhydride. Add 25 grams of NaH₂PO₄ dissolved in 100 ml of H₂O to the ammonium molybdate solution. Stir occasionally for 15 minutes and allow the precipitate to settle (~30 minutes). Filter through #42 Whatman paper. Wash the precipitate with 1% potassium nitrate and finally with distilled water. Dry the precipitate and paper at 110°C for 3-4 hours. Transfer the (NH₄)₃[PMo₁₂O₄₀] solid to a weighing bottle and store in a desiccator.

Sodium tetraphenylboron solution [3% NaB(C₆H₅)₄]. Add 30 grams of sodium tetraphenylboron to 800 ml of H₂O and stir for 30 minutes. Filter through #42 Whatman filter paper. Discard the insoluble material. Dilute the filtrate to 1 liter with H₂O.

Ethylene diamine tetraacetic acid solution [50% Na₄EDTA]. Dissolve 500 grams of Na₄EDTA in H₂O. Filter over glass wool. Discard insoluble material. Dilute the filtrate to 1 liter.

Cation Exchange column [Bio-Rex 40 (50-100 mesh)]. Transfer 500 grams of Bio-Rex 40 (50-100 mesh) to a 3 liter beaker. Add 2 liters of H₂O and stir for 30
minutes. Allow the resin to settle. Decant and discard the wash solution. Repeat the washing procedure with 2 liters of each of the following solutions:

1. 1N NaOH
2. H₂O (2 portions)
3. 1N HCl
4. H₂O (2 portions)

After the final wash, transfer the resin with water to a 1 liter polyethylene bottle for storage.

To prepare the cation exchanger, the column illustrated in Figure 2 is used. Fill the column with water and position a wad of glass wool at the bottom of the column with a glass rod. Transfer 15 ml of the wet-settled prepared resin to the column and allow it to settle. Place a second wad of glass wool at the top of the resin and with the stopcock open allow the water level to reach the top of the upper plug. Pass through 200 ml of 5% NaCl at a flow rate not exceeding 5 ml per minute. The column is now ready for the sample solution.

Preliminary Separations by Sodium Carbonate Fusion and Water Leaching of the Melt: Vegetation Ash and Soils

To the dried sample of up to 100 grams in a platinum crucible add 4 grams of Na₂CO₃ for each gram of sample and 1 ml of cesium carrier solution. Mix thoroughly. Fuse at 900°C. Remove melt and pulverize with a mortar and pestle. Transfer to a beaker and with stirring add 20 ml of hot H₂O for each gram of the original sample. Digest on a hot plate for 1 hour with stirring. Filter through a glass fiber filter paper. Wash with 5% Na₂CO₃. Discard the insoluble material. Combine the filtrate and wash solutions and proceed with cesium collection.
FIGURE 2. Ion Exchange Column
Preliminary Separations by Acid Dissolution and Calcium Phosphate Scavenging: Bone Ash and Milk Ash

Transfer 10 grams of the sample to a 250 ml beaker. Add 50 ml of HCl, 50 ml of H₂O, and 1 ml of cesium carrier solution. Boil the solution for 15 minutes. Filter by suction through a 9 cm glass fiber filter paper and wash the insoluble material with 75 ml of H₂O. Discard the carbonaceous residue.

Transfer the filtrate and wash solutions to an 800 ml beaker. Dilute to 500 ml with H₂O and add 2 ml of H₃PO₄. Adjust the pH to 10 with saturated NaOH. Allow the precipitate to settle and cool. Filter through a 15 cm glass fiber filter paper. Wash with 50 ml of H₂O. Discard the insoluble material. Transfer the filtrate and wash solutions to a 1 liter beaker and proceed with cesium collection.

Collection of Cesium with Ammonium Phosphomolybdate by Batch Extraction: All Samples

Neutralize the combined solutions from preliminary separations with HCl and add a sufficient excess of HCl to bring the pH of the solution to 1. Mechanically stir for 15 minutes and filter any precipitate that forms through a glass fiber filter paper. Wash with hot 1:10 HCl and discard the insoluble material.

To the combined filtrate and wash solutions add 1 gram of ammonium phosphomolybdate. Stir mechanically for 15 minutes. Filter with suction through a 5.5 cm glass fiber filter paper. Discard the filtrate. Dissolve the precipitate from the filter paper without suction by the addition of 10 ml of NH₄OH. Apply suction and wash the paper with 10 ml of H₂O. Combine the filtrate and wash solutions, and proceed with alkali separations.
Separation of Potassium and Rubidium by Reprecipitation of Cesium - Ammonium Phosphomolybdate Derivative: Rapid Analysis; 20-30% Loss of Cesium

Collect the dissolved APM fraction in a 40 ml centrifuge tube. Adjust the pH to ~1 with HCl. Centrifuge. Decant and discard the supernate. Dissolve the precipitate with 10 ml of NH₄OH. Adjust the pH to ~1 HCl. Centrifuge. Decant and discard the supernate. Wash the precipitate with 10 ml of 1N NH₄Cl (pH 2-3). Centrifuge. Decant and discard the wash solution.

Dissolve the precipitate by the dropwise addition of 10 ml of 6N NaOH. Dilute with H₂O to 20 ml. Add 1 gram CaCl₂ dissolved in 10 ml of H₂O. Adjust the pH to 7 with HCl. Centrifuge. Transfer the supernate to a 150 ml beaker. Wash with 10 ml H₂O. Discard precipitate. Transfer the wash solution to the 150 ml beaker and proceed with gravimetric determination.

Separation of Potassium and Rubidium by Selective Cation Exchange with Bio-Rex 40 Resin: 18 Hour Analysis; Quantitative for Cesium

Collect the dissolved APM fraction in a 90 ml centrifuge tube. Adjust the pH to 1-2 with HCl. Allow to stand for 15 minutes with occasional stirring. Centrifuge, decant, and discard the supernate. Wash down the sides of the centrifuge tube with ~5 ml H₂O, and dissolve the precipitate by the dropwise addition of saturated NaOH. Dilute the solution with H₂O to ~15 ml. Add 15 ml of 50% EDTA solution to the sample.

Pass the sample through a prepared Bio-Rex 40 (50-100 mesh) ion-exchange column (See - Column Preparation) at a flow rate not exceeding 1 ml per minute. Pass 100 ml of distilled water through the column at a flow rate not exceeding 2 ml per minute. Discard waste and wash solutions.
Elute K, Rb, and NH$_4$ with 1 liter of 0.1N HCl at a flow rate not exceeding 2 ml per minute. Discard the effluent. Elute cesium with 200 ml of 2N HCl at a flow rate not exceeding 5 ml per minute. Transfer to a 250 ml beaker and proceed with gravimetric determination.

**Gravimetric Determination of Cesium with Chloroplatinic Acid**

Evaporate the separated cesium fraction to about 5 ml. (If the wet chemical method of alkali separation has been used, add 5 ml of saturated NaOH to the solution prior to the evaporation and continue the digestion until NH$_3$ fumes are no longer evolved.) Transfer to a 40 ml centrifuge tube. If necessary, acidify the solution with HCl. Cool in an ice bath. Add with stirring 4 ml of 10% H$_2$PtCl$_6$ and allow the sample to settle for 2 hours. Filter through a weighed 2.4 cm glass fiber filter paper. Wash with H$_2$O. Discard the filtrate and wash solutions. Dry the precipitate for 1 hour at 110°C. Weigh, mount, and beta count.

**Gravimetric Determination of Cesium with Sodium Tetraphenylborate**

Evaporate the separated cesium solution to about 5 ml and transfer with H$_2$O to a 90 ml centrifuge tube. Adjust the pH to 12.5 with saturated NaOH solution and add 10 ml of 3% sodium tetraphenylboron solution. (If the wet chemical alkali separation has been used, add 20 ml of 37% formaldehyde to complex NH$_4^+$ ions prior to the addition of the NaTPB solution.) Allow the sample to stand for 15 minutes with occasional stirring. Filter through a 2.4 cm glass fiber filter paper. Wash with H$_2$O and a few drops of 0.1% Aerosol OT solution. Discard the filtrate and wash solutions. Dry the precipitate for 1 hour at 110°C, weigh, mount, and beta count.
RESULTS AND DISCUSSION

The loss of cesium during individual steps of the procedure was determined by processing 100 gram aliquots of soils 10783 and 10784 and 10 gram aliquots of bone B0126 with about 1 μc of Cs-137 added to each. Average recovery data obtained for about 50 analyses by gamma counting the different fractions are listed in Table 2.

Detailed data for the cation exchange system were obtained by processing stock solutions containing from 1 to 60 mg of Rb⁺, from 1 to 30 mg of Cs⁺ and either 1 μc of Rb-86 or 1 μc of Cs-137 through a sample column. An illustration of these findings is presented in Figure 3. The efficiency of the wet chemical method for alkali separation was

![Figure 3: Cation Exchange Separation of Cs and Rb](image-url)
similarly measured. These results are listed below:

\[
\begin{array}{l|cc}
\text{Process} & \text{Cs-137} & \text{Rb-86} \\
\hline
\text{After APM Extraction} & 93 & 20 \\
\text{After Reprecipitation} & 85 & 12 \\
\text{After NH}_4\text{Cl Wash} & 78 & <5 \\
\end{array}
\]

The assumption has been made in all of the analyses that the normal cesium content of environmental samples is negligible with respect to the amount of cesium added as carrier. To test this hypothesis, at least one analysis was performed on each of the experimental matrices listed in Table 1 without the addition of carrier. In no case was a significant recovery of cesium obtained. In soils 60424 and 601074 where proximity to the sea might be expected to cause high cesium and rubidium concentrations (16), the maximum weight of the cesium tetraphenylboron or chloroplhatinate derivatives obtained was 0.8 mg.

Decontamination from natural and artificial radioactivities was measured by processing soils C-7164, C-3188, ID and IE (Table 1) through the procedure. In the case of the fission product blanks, no gamma or beta activity was detected in the final cesium precipitates. The results of the old and fresh fission product determinations (illustrated in Figures 4 and 5) show no significant gamma activities remaining after the phosphomolybdate separation which are not attributable to cesium fission products.

ACKNOWLEDGMENTS

The assistance of L. T. Alexander and J. S. Allen of the U. S. Department of Agriculture Soil Survey Laboratory in fusing most of the experimental soils, of C. Lund and C. S. Maupin of Reynolds Electrical & Engineering Co. in collecting the Nevada soils and of M. S. Feiner and J. Catania of the Health and Safety Laboratory in performing some of the investigative analyses is gratefully acknowledged.
FIGURE 4: RADIOACTIVITY IN SOIL I

A  Y Spectrum of Dried Soil counted July 12, 1962
B  Y Spectrum of APN Fraction counted July 17, 1962

FIGURE 5: RADIOACTIVITY IN SOIL II
Close-in Fallout from Ebbet, Mar. 16, 1962

A  Y Spectrum of APN Fraction counted July 13, 1962
B  Y Spectrum of APN Fraction counted Oct. 10, 1962
C  Oct. 10th Spectrum minus Estimated Ca134 Spectrum
REFERENCES


OBSERVED EFFECTIVE HALF LIFE OF TRITIUM
AT THE SAVANNAH RIVER PLANT

H. L. Butler
E. I. du Pont de Nemours and Co.
Savannah River Plant
Aiken, S. C.

Two hundred-sixty assimilations of tritium, approximating one millicurie, have occurred at the Savannah River Plant in the past five years. Half life observations, and efforts to correlate these values with variables, are discussed.
**Introduction**

The Savannah River Plant (SRP) is the center of tritium production in the United States. Quantities of tritium, sufficient to present a health hazard to operating personnel, are produced by the irradiation of lithium in the production program and as an unwanted by-product from neutron irradiation of heavy water moderator in the reactors.¹ Radiological protection from tritium is complicated by the low average energy of the emitted beta particles (5.7 kev) and by the ease with which it is assimilated. Since tritium is distributed equally in all body fluids, it is considered a whole body irradiator. Doses from this source must therefore be added to those from external sources for computation of whole body exposure; this is accomplished through use of urinalysis data, including the individual's biological half life. In 1961, the total dose contributed by tritium to all employees working in the reactor areas amounted to 133 rems or 16% of their total whole body dose. This paper summarizes biological half-life data from more than 260 cases in which the tritium concentration in urine was from 20 to 110 µc per liter.

**Discussion**

**Bio-Assay Program**

At SRP, personnel provide urine samples following work in areas where tritium may be assimilated. The number of samples analyzed currently approximates 80,000 per year. Samples are analyzed and the results are available prior to the time an employee returns for his next shift of work. They are analyzed in replicate when the results are 10 µc per liter or higher. Most urinalysis data were obtained using liquid scintillation counting, although some early values were obtained using a hydrogen generator (calcium-urine reaction) and measuring with a vibrating reed electrometer. In the current method of analysis,² one milliliter of urine is added to scintillation materials which are dissolved in dioxane. The lower limit of detection for the standard one minute count is one µc of tritium per liter of urine. Whenever a urinalysis result exceeds 20 µc per liter, additional samples are obtained to determine the individual's biological half life for tritium. For results between 5 and 20 µc per liter, a 12 day biological half life is used for computing dose; on this basis, a dose of 45 mrem results from a 5 µc per liter uptake.

**Measurement of Effective Half Life**

As early as 1934, Von Hevesy and Hofer³ measured the body water turnover rate of a single subject (using deuterium oxide) and reported a value of 9 to 10 days. Other investigators have obtained the
comparable values shown in Table 1. Some references, however, list values as high as 19 days as the effective half life. Data by Foy and Schnieden were obtained on 10 male students in tropical Nigeria; this may account for their value of 7.5 days. Richmond, Langham, and Trujillo carried out comparative studies on seven mammalian species (including man) in an effort to relate water turnover rate with body weight. Using tritiated water, they found the rate to vary interspecifically as the 0.8 power of body weight.

Effective half lives in 260 cases of tritium assimilation at SRP were reviewed and an average half life value of 9.6 days ± 4.3 days, at the 90% confidence level, was obtained (see figure 1).

Table 1. Biological Half Life

<table>
<thead>
<tr>
<th>Isotope Used</th>
<th>Biological Half Life, days</th>
<th>Number of Subjects</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDO</td>
<td>9 - 10</td>
<td>1</td>
<td>1934</td>
<td>Von Hevesy and Hofer</td>
</tr>
<tr>
<td>HDO</td>
<td>9.3 ± 1.5</td>
<td>21</td>
<td>1950</td>
<td>Schloerb and others</td>
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<tr>
<td>HTO</td>
<td>9 - 14</td>
<td>8</td>
<td>1951</td>
<td>Pinson and Anderson</td>
</tr>
<tr>
<td>HTO</td>
<td>5 - 11</td>
<td>20</td>
<td>1957</td>
<td>Fallot and others</td>
</tr>
<tr>
<td>HTO</td>
<td>9.3 - 13</td>
<td>8</td>
<td>1957</td>
<td>Pinson and Langham</td>
</tr>
<tr>
<td>HTO</td>
<td>7.5 ± 1.9</td>
<td>10</td>
<td>1960</td>
<td>Foy and Schnieden</td>
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<tr>
<td>HTO</td>
<td>9.5</td>
<td>5</td>
<td>1962</td>
<td>Richmond and others</td>
</tr>
</tbody>
</table>

Factors Influencing Half Life

It is pertinent to consider some of the variables which influence biological half life. Pinson and Langham found a 10 day half life when water intake was 2.7 liters per day; however, when water intake was increased to 12.8 liters per day, the half life was reduced to 2.4 days. In 8 cases of ad libitum water intakes, they observed values ranging from 4.3 to 13 days. By comparison, a range of 4 to 18 days was found at SRP for ad libitum water intake. As for incorporation of tritium into organic constituents, sufficient data were collected by Thompson and Pinson and Langham to be reasonably assured that this factor is relatively insignificant and that essentially all tritium entering the body is eliminated. The exchange of tritium with labile hydrogen atoms occurs only to a limited extent, perhaps no more than 1 to 4% according to these investigators.

Ambient Temperature vs Half Life

Comparisons were made of half life with mean temperature at the time of tritium uptake. Our data indicated shorter half lives where assimilations occurred in the warmer months and longer half lives when uptakes occurred during cooler periods (see Tables 2 and 3). Average mean temperature for the SRP area for the past four years was 63°F compared to an 80°F average for southern Nigeria where the 7.5 day average half life was found.
Fig. 1

**DISTRIBUTION OF HALF LIVES**

- Tb, Number of Days
- Frequency
Table 2. Seasonal Half Life

<table>
<thead>
<tr>
<th></th>
<th>Spring</th>
<th>Summer</th>
<th>Fall</th>
<th>Winter</th>
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<tbody>
<tr>
<td>Average Biological Half Life, days</td>
<td>8.3</td>
<td>8.3</td>
<td>10.4</td>
<td>10.4</td>
</tr>
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</table>

Table 3. Monthly Half Life

<table>
<thead>
<tr>
<th></th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>Aug</th>
<th>Sept</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
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</thead>
<tbody>
<tr>
<td>Avg Biological half life, days</td>
<td>10.0</td>
<td>9.5</td>
<td>11.0</td>
<td>8.8</td>
<td>7.8</td>
<td>8.0</td>
<td>6.5</td>
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<td>9.3</td>
<td>9.3</td>
<td>10.9</td>
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<td>Mean Temp, °F</td>
<td>44</td>
<td>48</td>
<td>50</td>
<td>63</td>
<td>72</td>
<td>77</td>
<td>80</td>
<td>80</td>
<td>76</td>
<td>66</td>
<td>56</td>
<td>48</td>
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<tr>
<td>No. of Cases</td>
<td>36</td>
<td>22</td>
<td>38</td>
<td>30</td>
<td>13</td>
<td>13</td>
<td>11</td>
<td>12</td>
<td>11</td>
<td>20</td>
<td>29</td>
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</table>

EFFECT OF AMOUNT ASSIMILATED ON HALF LIFE

Twenty SRP uptakes ranging from 50 to 110 μc per liter showed an average half life of 8.3 days; 120 uptakes in the 20 to 25 μc per liter range averaged 9.9 days. However, this difference cannot be attributed to the higher tritium uptake or be considered significant. It is more likely due to each employee voluntarily increasing his liquid intake in the cases of higher uptakes. There were no instances involving forcing of fluids or use of diuretics by the Plant Medical Department.

VARIATIONS OF HALF LIFE IN THE INDIVIDUAL

The data for employees who experienced more than one assimilation were also reviewed. In six cases, individual employees had three or more uptakes. The data, shown in Table 4, indicates no consistency in the rate of elimination.

Table 4. Variations of Half Life Within Individuals

<table>
<thead>
<tr>
<th>Employee</th>
<th>μc/l</th>
<th>Effective Half Life, days</th>
<th>Date of Uptake</th>
<th>Employee</th>
<th>μc/l</th>
<th>Effective Half Life, days</th>
<th>Date of Uptake</th>
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<td>RKB</td>
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<td>37</td>
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<td>July 1961</td>
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<td>12</td>
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<td>30</td>
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<td>Dec 1957</td>
<td></td>
<td>45</td>
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<tr>
<td>CM</td>
<td>25</td>
<td>Dec 1960</td>
<td></td>
<td>34</td>
<td>11.0</td>
<td>March 1960</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>12</td>
<td>Jan 1961</td>
<td></td>
<td>38</td>
<td>13.5</td>
<td>Aug 1960</td>
<td></td>
</tr>
<tr>
<td>GAL</td>
<td>24</td>
<td>7.5</td>
<td>March 1960</td>
<td>26</td>
<td>12</td>
<td>Sept 1960</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>8</td>
<td>Jan 1961</td>
<td></td>
<td>22</td>
<td>10.5</td>
<td>March 1961</td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>6.5</td>
<td>June 1961</td>
<td></td>
<td>22</td>
<td>9</td>
<td>Oct 1961</td>
<td></td>
</tr>
</tbody>
</table>
In seven other cases where two separate uptakes occurred, four employees showed essentially the same half life for each assimilation while the other three showed half lives which varied by as much as 2 to 1.

BODY WEIGHT VS HALF LIFE

Weight was another variable studied in this group of assimilations; data are shown in Table 5. Our weight - half life relationships do not confirm the power function of 0.8 body weight found interspecifically by Richmond and coworkers. The fact that no control of other variables existed may account for the lack of confirmation.

<table>
<thead>
<tr>
<th>Average Weight for Group, lb</th>
<th>Number in Group</th>
<th>Average Half Life, days</th>
</tr>
</thead>
<tbody>
<tr>
<td>130-139</td>
<td>8</td>
<td>9.4</td>
</tr>
<tr>
<td>140-149</td>
<td>23</td>
<td>8.6</td>
</tr>
<tr>
<td>150-159</td>
<td>37</td>
<td>9.9</td>
</tr>
<tr>
<td>160-169</td>
<td>47</td>
<td>10.1</td>
</tr>
<tr>
<td>170-179</td>
<td>51</td>
<td>9.3</td>
</tr>
<tr>
<td>180-189</td>
<td>39</td>
<td>9.5</td>
</tr>
<tr>
<td>190-199</td>
<td>23</td>
<td>10.0</td>
</tr>
<tr>
<td>200-209</td>
<td>12</td>
<td>10.7</td>
</tr>
<tr>
<td>210-219</td>
<td>8</td>
<td>11.4</td>
</tr>
</tbody>
</table>

AGE INFLUENCE

The comparison of half life with age was more consistent than other variables which were investigated. The average biological half life was computed for various age groups; data indicated a decreasing half life with increasing age (see figure 2). No references were noted in the literature of similar comparisons nor is an explanation attempted, although, in renal function studies, Miller and Shock obtained data on 29 subjects which showed impaired ability of the kidneys of older individuals to perform osmotic work. The higher turnover rate was thought by these investigators to be due to decreasing production of antidiuretic hormone.

Conclusions

An average biological half life for tritium of 9.6 days ± 4.3 days (90% confidence limit) was found in 260 cases at the Savannah River Plant. Slightly higher values were observed with lower ambient temperatures and correspondingly lower half life values were noted at higher temperatures. There appears to be evidence of a shorter half life with increasing age.
Fig. 2

BILOGICAL
HALF LIFE

vs AGE

- 44 -
References


In support of the N. S. SAVANNAH Medical Program, shipboard procedures have been established for detecting significant exposures to internal radioactive contamination and for estimating radionuclide deposition in body organs. As a result of space and equipment restrictions on board ship, all procedures were necessarily simplified so as to entail a minimum of processing. Direct counting of raw urine samples by gamma ray spectrometry was found to provide adequate sensitivity for detecting significant chronic or acute internal exposures to gross mixtures of radioactive corrosion products or fission products. The employment of a collimated 3" x 3" NaI(Tl) crystal to scan selected portions of the body offers sufficient sensitivity to provide estimates of organ burdens. Lung burdens of five per cent of the maximum permissible levels for individual major corrosion or fission products may be detected easily.
INTRODUCTION

The objective of this project was to develop a comprehensive bio-assay program for the N. S. SAVANNAH Medical Department. In recognition of the limitations in space and equipment aboard ship, all procedures were necessarily simplified so as to entail a minimum of processing. After a potential internal exposure there is no way to evaluate the actual exposure except to make instrument measurements directly of the gamma radiation penetrating to the outside of the body, or to perform quantitative radioisotopic analysis upon specimens of materials originating in the body. Usually, samples are collected of all available body materials (serial specimens of blood, urine, and feces), analyses are performed by the most precise methods, multiple whole body counter measurements are made, and a large crew of individuals are assigned to analyze both the field and laboratory data. Nevertheless, the derivation of a valid estimate of internal dose is a most difficult task even under the best conditions. So, when reliance must be placed upon a limited number of measurements, and when the analysis techniques must be somewhat gross, the accuracy of dose estimate is generally very poor. Therefore, for significant cases of internal exposure, there is no substitute for detailed analysis using every available facility.

In view of space and other limitations, the first step in establishing a comprehensive bio-assay program for the N. S. SAVANNAH was directed toward developing a procedure with which significant cases of internal exposure could be recognized. Once the most serious exposures have been recognized, a more intensive effort may be applied to obtain estimates of internal dose.
SCREENING

The initial approach to providing a screening procedure for shipboard use was to count specimens of raw urine directly on an NaI(Tl) crystal and to determine efficiency factors and limits of detectability for the major corrosion and fission products. Indications were that the most likely internal exposure incidents aboard the N. S. SAVANNAH would involve radioactive corrosion products. Data from SM-1, similar in many respects to the SAVANNAH reactor, show that soon after startup the predominant corrosion product is Co$^{^{58}}$ (about seven times as much Co$^{^{58}}$ as Co$^{^{60}}$). The other major corrosion products, Cr$^{^{51}}$, Fe$^{^{59}}$, and Mn$^{^{54}}$ are in the same order of concentration as Co$^{^{60}}$. Thus, if Co$^{^{58}}$ is being eliminated in the urine, it may be assumed that exposure to a gross mixture of corrosion products has occurred. By the same token, if Cs$^{^{137}}$ is being eliminated in the urine, a fission product exposure would be suspected.

Equipment and Procedure

All development work at ORNL was done with the N. S. SAVANNAH counting equipment. A 128-channel analyzer and one 2" x 2" well-type NaI(Tl) crystal was already available for use aboard the SAVANNAH. A solid 3" x 3" NaI(Tl) crystal was purchased later to provide greater sensitivity. Aliquots (100 ml) of urine were measured into a 3-inch diameter plastic container and placed on top of the crystal for counting. A positive net count in the channels used for Co$^{^{58}}$ and Co$^{^{60}}$ is suggestive of a corrosion product exposure. A positive net count in the Cs$^{^{137}}$ channel suggests a fission product exposure. By counting the raw urine in this manner the limits of detection are sufficiently low to detect a maximum permissible exposure to a gross mixture of soluble corrosion and fission products. This, of course, presupposes that a significant fraction of the ingested radionuclides are excreted in the urine.
Although no applicable human data were available at the beginning of the program, later an otherwise insignificant exposure incident provided some insight into the problems of assessing internal exposure to corrosion product mixtures. Following an accidental inhalation exposure of two ORNL employees to a mixture of corrosion products, urinalysis results were negative except for the first 24-hour collection. On the other hand, collimated chest counts with a NaI crystal continued to show detectable quantities of Co\textsuperscript{60} for more than a year following the incident. Thus, it was felt that an alternate procedure should be available for use aboard the N. S. SAVANNAH.

**ESTIMATING ORGAN BURDENS BY EXTERNALLY SCANNING SELECTED AREAS OF THE BODY**

The most direct procedure for use in estimating body burdens of gamma emitting nuclides is to measure the gamma radiation penetrating to the outside of the body from internal deposits. Where applicable, direct measurement can yield a less ambiguous result than is available using indirect methods such as excretion analysis. By using a collimated crystal the location and extent of internal deposits may be estimated. After an inhalation exposure to an insoluble nuclide, the urinary excretion may be a poor indication of the actual lung deposit. It is anticipated that the most likely exposure incidents aboard the N. S. SAVANNAH will involve corrosion products circulating in the primary coolant. Data from the SM-1 reactor show that the largest fraction of the circulating activity in the primary loop is due to filterable Co\textsuperscript{58} and Co\textsuperscript{60}. An inhalation exposure to this relatively insoluble mixture can be evaluated most readily by measuring the gamma rays penetrating to the outside of the body.
Equipment and Procedure

The 128-channel analyzer and 3" x 3" NaI(Tl) crystal are utilized for external measurements. The crystal is mounted in an iron shield which has a removable top. When the top is removed, gamma radiation originating directly over the crystal is detected while the walls of the shield effectively collimate against gamma radiation originating elsewhere. A person lying on a cot placed over the shield can be scanned for gamma emitting deposits by moving the cot so as to place any selected area of the body directly over the crystal.

Efficiency Factors

Sources were placed inside a pressed-wood phantom and counted in order to simulate conditions of shielding and geometry for the human body. Efficiency factors (counts per disintegration) were established for the major corrosion products and Cs$^{137}$ (Table 1).

<table>
<thead>
<tr>
<th>Corrosion Product</th>
<th>Energy (Mev)</th>
<th>Channel Number (inclusive)</th>
<th>Efficiency (Per Cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^{51}$</td>
<td>.32</td>
<td>20 - 26</td>
<td>.040</td>
</tr>
<tr>
<td>Co$^{58}$</td>
<td>.81 (.51)</td>
<td>53 - 69</td>
<td>.212</td>
</tr>
<tr>
<td>Co$^{60}$</td>
<td>1.17, 1.33</td>
<td>79 - 106</td>
<td>.373</td>
</tr>
<tr>
<td>Fe$^{59}$</td>
<td>1.10, 1.29</td>
<td>79 - 106</td>
<td>.161</td>
</tr>
<tr>
<td>Cs$^{137}$</td>
<td>.662</td>
<td>42 - 58</td>
<td>.200</td>
</tr>
</tbody>
</table>

When a composite spectrum is obtained by placing all of the sources in the phantom at one time, the scatter from higher energy peaks must be subtracted from those of lower energy in order to evaluate the net count due to each primary peak (Table 2).
Table 2

<table>
<thead>
<tr>
<th>Band A (Fe$^{59}$ + Co$^{60}$)</th>
<th>= net count in channels 79 - 106</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band B (Co$^{58}$)</td>
<td>= net count in channels 53 - 69</td>
</tr>
<tr>
<td>Band C (Cs$^{137}$)</td>
<td>= net count in channels 42 - 58</td>
</tr>
<tr>
<td>Band D (Cr$^{51}$)</td>
<td>= net count in channels 20 - 26</td>
</tr>
</tbody>
</table>

Fe$^{59}$ + Co$^{60}$ = net count in Band A

Co$^{58}$ = Band B - (.59 x Band A)

Cs$^{137}$ = Band C - (.64 A + .65 B)

Cr$^{51}$ = Band D - (.66 A + .75 B + .55 C)

The energies of Fe$^{59}$(1.10, 1.29 Mev) and Co$^{60}$(1.17, 1.33 Mev) are so close that it is difficult to distinguish them when both are present in a source. It is conservative to assume everything in this energy range is due to Fe$^{59}$.

Alternatively, the following calculation can be based on the peak to peak ratio of Fe$^{59}$ and of Co$^{60}$ (Figure 1).

- Band E = channels 78 - 85 net count
- Band F = channels 94 - 101 net count
- Band E/Band F = 1.95 for pure Fe$^{59}$
- Band E/Band F = .660 for pure Co$^{60}$
- Band E/Band F = R for mixture (0.66 ≤ R ≤ 1.95)

\[ K = \frac{1.95 - R}{1.95 - .66} \] = fraction of count due to Co$^{60}$

\[ (0 \leq K \leq 1) \]

The factor K can be applied to the net count in channels 79 - 106 to produce an estimate of the count due to Co$^{60}$. This product subtracted from the net count in channels 79 - 106 gives the estimated count due to Fe$^{59}$. The disintegration rate for each may then be obtained by dividing by the time and by the appropriate efficiency factors.

Figure 1 shows the gamma spectrum obtained by placing five different radionuclides in a pressed-wood phantom and
COMPOSITE SPECTRUM
CHEST PHANTOM
CONTAINING
CORROSION PRODUCT MIXTURE PLUS
CESIUM—137

ADDED FOUND
\( \mu \text{C} \) \( \mu \text{C} \)
\( ^{60} \text{Co} \) 1.75 1.81
\( ^{54} \text{Fe} \) 1.73 1.69
\( ^{137} \text{Cs} \) 1.82 1.75
\( ^{117} \text{Cd} \) 2.00 2.05
\( ^{51} \text{Cr} \) 36.4 43.0

BACKGROUND—3 X 3" NA I CRYSTAL
(REACTOR 100% POWER)

FIGURE 1
counting for 13.1 minutes at 13.3 KeV/channel. Each nuclide was contained in four vials of equal concentration and the total of 20 vials was distributed in the phantom so as to simulate distribution in the lung.

Sample Calculations

Net c/m in Band E = 6377
Net c/m in Band F = 6165
E/F for mixture = 1.03
E/F for pure Fe$^{59}$ = 1.95
E/F for pure Co$^{60}$ = .660

$$K = \frac{1.95 - 1.03}{1.95 - .66} = .713$$

71.3% of total counts are due to Co$^{60}$,

(28.7% of total counts are from Fe$^{59}$).

Total count rate in channels 79 - 106 = 20,841 c/m

$$0.713 \times 20,841 = 14,860 \text{ c/m Co}^{60} \ (5,981 \text{ c/m Fe}^{59})$$

Efficiency for Co$^{60}$ in channels 79 - 106 = .373 per cent

$$14,860/.00373 = 3.98 \times 10^6 \text{ d/m} = 1.81 \mu\text{c Co}^{60}$$

(1.69 \mu\text{c Fe}^{59})

These calculated values compare well with the actual amounts of 1.75 \mu\text{c Co}^{60} \ and 1.73 \mu\text{c Fe}^{59} \ in the sources.

Calculation of the other radionuclides represented in the spectrum is done by referring to Tables 1 and 2.

<table>
<thead>
<tr>
<th>Band</th>
<th>Isotope</th>
<th>Net c/m</th>
<th>Corrected for Scatter</th>
<th>Estimated (\mu\text{c} )</th>
<th>Known Amounts (\mu\text{c} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Co$^{60}$</td>
<td>20,841</td>
<td>20,841</td>
<td>1.81</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>Fe$^{59}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Co$^{58}$</td>
<td>20,457</td>
<td>8,182</td>
<td>1.75</td>
<td>1.82</td>
</tr>
<tr>
<td>C</td>
<td>Cs$^{137}$</td>
<td>27,788</td>
<td>9,044</td>
<td>2.05</td>
<td>2.00</td>
</tr>
<tr>
<td>D</td>
<td>Cr$^{51}$</td>
<td>62,720</td>
<td>37,854</td>
<td>42.6</td>
<td>36.4</td>
</tr>
</tbody>
</table>
MEASUREMENT OF Na\textsuperscript{24} IN BLOOD

The measurement of Na\textsuperscript{24} produced in the blood stream by neutron irradiation of the human body has been shown to be a useful technique for estimating total doses received by individuals as a result of nuclear accidents\textsuperscript{(1)}. The \((n,\gamma)\) reaction in Na\textsuperscript{23} produces Na\textsuperscript{24}, which emits a 1.38 Mev gamma ray in cascade with a 2.76 Mev gamma ray for each disintegration. Blood levels of Na\textsuperscript{24} are taken to be a good indication of the average neutron flux to which a subject has been exposed. However, in order to evaluate properly the total exposure, one must know the neutron spectrum, as well as the associated gamma dose.

In June 1958 five people were involved in a criticality incident at the Oak Ridge Y-12 Plant\textsuperscript{(1)} and the Na\textsuperscript{24} in their blood was thoroughly investigated. The flux ratio of fast neutrons to thermal neutrons for this accident was about 2:1. In October 1958 six people were exposed in a nuclear excursion in Yugoslavia\textsuperscript{(2)}. The fast neutron to thermal neutron flux ratio for this case was about 0.25:1. It has been suggested that the neutron ratios for these two incidents may well represent opposite extremes for most nuclear incidents that may occur in the future. Na\textsuperscript{24} in the blood following the predominantly fast neutron exposure at Y-12 was found to be \(6.0 \times 10^{-6} \mu\text{c/ml blood/rad neutron}\) (extrapolated to time of exposure, \(t = 0\)). Blood from personnel exposed to the predominantly thermal neutron flux in Yugoslavia contained \(2.6 \times 10^{-5} \mu\text{c Na}\textsuperscript{24}/\text{ml blood/rad neutron}, (t = 0)\). Since it is impossible to predict the neutron spectrum for all possible incidents aboard the N. S. SAVANNAH, it is assumed to be within the ranges of the Y-12 and Yugoslavia cases.

The significance of a neutron exposure may be approximated quickly by referring to Figure 2 and the examples (p. 56). The
SODIUM-24 COUNT RATE IN BLOOD SERUM AS A FUNCTION OF TIME SINCE HUMAN EXPOSURE TO NEUTRONS (NS SAVANNAH 313 CRYSTAL-STD. GEOMETRY)

NET c/m IN THIS RANGE INDICATE GREATER THAN 10 RAD NEUTRON EXPOSURE

0 EXAMPLE NO.3
COUNTING TIME = 13.1 MIN.
KEV/CHANNEL = 27.3
Na24 2.76 MeV. PHOTOPEAK BAND
No24 2.76 MeV. PHOTOPEAK BAND
CHANNELS 97 THRU 106 —
(i.e. 2.621 MeV. TO 2.894 MeV.)
BACKGROUND IN BAND =
27 COUNTS Per MIN. (20° = 2.9 c/m)

0 EXAMPLE NO.2
IN THIS RANGE INDICATE 3 - 40 RAD NEUTRON EXPOSURE
RATIO OF GAMMA RADS TO NEUTRON RADS = 3.8

0 EXAMPLE NO.1
NET COUNTS Per MIN. IN THIS RANGE INDICATE LESS THAN 10 RAD. NEUTRON EXPOSURE
RATIO OF GAMMA RADS TO NEUTRON RADS

NET COUNTS Per MIN. IN THIS RANGE ARE WITHIN TWO STANDARD DEVIATIONS OF THE BACKGROUND
(95% CONFIDENCE LEVEL)

FIGURE 2
associated calculations are based on the assumption that the parameters pertinent to any unknown exposure fall within the range of the exposures from which these two curves were obtained.

Example 1 -- 30 ml of serum counts 15 c/m, 15 hours after exposure. The exposure can be assumed to be light, probably less than 10 rad neutron.

Example 2 -- 30 ml of serum counts 50 c/m, 30 hours after exposure. The exposure can be assumed to be in the moderate range, probably approaching 40 rad for a fast neutron exposure and nearer 10 rad for a thermal neutron exposure.

Example 3 -- 30 ml of serum counts 100 c/m, 30 hours after exposure. Possibilities range from mild to significant exposure. Fast neutron exposure would be ≈ 70 rad exposure. Exposure to a thermal flux (Yugoslavia case) would correspond to ≈ 17 rad.

A more precise estimation of the dose can be made by knowing the neutron flux of the exposure. This information can best be obtained from film badges and threshold detectors. The gamma dose must be known also to estimate the total exposure. The gamma dose to neutron dose ratio was 3.8 for the Yugoslavia incident and 2.8 for the Y-12 excursion. Therefore, by assuming the worst likely combinations of gamma and neutrons, any blood activity below the Y-12 curve would still indicate a mild to moderate exposure range.
REFERENCES


A METHOD FOR DETERMINING LOW LEVEL ALPHA ACTIVITY FROM AMERICIUM$^{241}$, CURIUM$^{244}$, AND CALIFORNIUM$^{252}$ IN BIOLOGICAL MATERIALS

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Lawrence Radiation Laboratory
University of California
Berkeley 4, California

The nuclides are coprecipitated with lanthanum fluoride. Separation is effected on specially designed small columns, using a series of three different ion exchange resins. The final eluate is collected on platinum and counted directly by pulse height analysis.

The method is sensitive enough to detect activities as low as 0.3 dpm, and is applicable to both urine and tissues.

Volumes involved in the chromatographic steps are small, so that separation can be carried out in about two hours.

Identification of nuclides is made by pulse height analysis, so that the method is useful when a single nuclide is present or when two or more are present in combination.
DISCUSSION

The following procedures are applicable to any actinide element which is carried by BiPO₄ precipitation.* These include: actinium, thorium, neptunium, plutonium, americium, curium, and californium.

The method may be used for determinations in urine, feces, or tissues.

The activity is precipitated with BiPO₄ and then separated by ion exchange chromatography. The final eluate is electro-deposited on stainless steel. Preparations may be counted for gross activity on a low background proportional alpha counter; for identification of radionuclides by pulse height analysis; or they may be radioautographed for alpha track counting.

Recoveries vary somewhat for the several nuclides, but are in the range 75 - 90 ± 3%.

The method has a detection limit of 0.2 dpm at the 99% confidence level.

The procedures, exclusive of counting time, require about 14 hours after ashing of the sample is complete.

Urine and feces are prepared for processing by wet ashing with nitric acid. Tissues are dry ashed for 24 hours in an oven at 100° C followed by 24 hours in a muffle furnace at

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* Our own experience with this method is limited to Am²⁴¹, Cm²⁴⁴, and Cf²⁵². These nuclides have been used separately and in combination.
In order to produce a pure white ash, one or two digestions with 10 ml portions of hot nitric acid may be necessary.

The white ash is taken up in 2N nitric acid and centrifuged to remove any undissolved material. The activity is then precipitated with BiPO₄ at pH 1.7 and 80 - 85°C with continual stirring for one hour (1). One ml of Bi(NO₃)₃ containing 10 mg Bi⁺⁺⁺ per ml and 0.5 ml H₃PO₄ are used for the precipitation.

The precipitate is dissolved in 0.5 ml of 8N HCl and placed on an anion exchange column 3 mm in diameter and packed to a height of 8 cm with Dowex 1 x 8 200 - 400 mesh in the chloride form (2). The effluent is collected and the column washed three times with 0.5 ml portions of 8N HCl. The washings are added to the effluent. The combined effluent is evaporated to dryness and the residue is dissolved in 0.5 ml 0.05N HCl. This is put on a column 3 mm in diameter and packed to a height of 5 cm with Dowex 50 x 4 200 - 400 mesh resin in the hydrogen form. The column is equipped with a glass jacket (see Fig. 1), and is operated at a temperature of 87°C by means of boiling trichloroethylene in a flask attached to the jacket of the column and to a reflux condenser.

The effluent from this column operation is discarded, and the column is washed with 0.65 ml 2N HCl. The effluent from the wash is also discarded. The activity is then eluted with 6N HCl. The first three drops are discarded and the next 30 drops are collected in a 10 ml beaker.

The eluate is evaporated to incipient dryness without boiling, and 0.3 ml H₂SO₄ is added and heated to dense white fumes (3). After cooling, the contents of the beaker are transferred with copious rinsing with distilled water to an
HEATED ION EXCHANGE COLUMN

Air-cooled reflux condenser

13 \mu liter drop Pt tip

Trichloroethylene

FIGURE 1
electrodeposition cell equipped with a 10 mil stainless steel disc and a platinum electrode (4). The volume in the cell is brought to 10 ml with distilled water and one drop of 1% methyl red is added. The sample is titrated with NH₄OH to the first permanent yellow, and is then titrated back to one drop on the red side with 1.5N H₂SO₄. Electrodeposition is carried on for 5 hours at 12 V and 180 ma. Before turning off the current, one drop of NH₄OH is added and electrodeposition is continued for one minute. The contents of the cell is decanted and the cell rinsed several times with distilled water. The stainless steel disc is removed and washed with distilled water and acetone and dried in air. It is then flamed to cherry red.

Gross alpha activity may be determined by counting in a low background proportional alpha counter. With low activities, counts should be made for at least 120 minutes.

Identification of nuclides is accomplished by means of a counter equipped with a multi-channel alpha energy analyzer. Peaks are identified by comparison with the peaks of two or more nuclides used as standards. In this work we have used an alpha grid chamber and an RIDL counter with a one hundred channel analyzer. In order to develop discernible peaks with low activities, it has been necessary to count the samples for at least 10 hours. We have found this system to have about the same geometry as our proportional alpha counter, i.e., approximately 50%. At the 99% confidence level our detection limit is 0.2 dpm, based on three times the standard error of
background counts. We are now about to experiment with semiconductor detectors in the hope that their superior resolving capacity and their insensitivity to background conditions will enable us to lower our detection limit and otherwise to increase counting efficiency.

In this work we have used activities of 0.5 dpm or less. Our recoveries have been: Am$^{241}$, 90 ± 3%; Cm$^{244}$, 75 ± 3%; Cf$^{252}$, 88 ± 3%. In the tissues of mice which had been given Am$^{241}$ and Cf$^{252}$ in combination (5), the Am$^{241}$/Cf$^{252}$ ratios found by our method were in close agreement with those obtained by gamma counting.

The authors acknowledge with appreciation the generous cooperation of Dr. Eugene Huffman of Lawrence Radiation Laboratory who provided us with chromatographic procedures which we have modified for use with biological materials.

REFERENCES

2. Huffman, Eugene, Personal communication.
The high specific activity of Am\textsuperscript{241} and the attendant lower value of the maximum permissible body burden for this isotope creates a need for the identification and evaluation of both its excretion and retention in the presence of concurrent plutonium.

A relatively simple and reliable urinalysis procedure for isolation and determination of Am\textsuperscript{241} in the presence of other heavy elements, particularly uranium and plutonium, has been developed.

Discussion of the method covers utilization of carrier techniques for isolation of americium from bulk sample and solvent extraction with di-2-ethylhexylphosphoric acid for separation from other actinides.

Control data on urine samples "spiked" with a standardized mixture of americium and heavy element contaminants resulted in an average recovery of approximately 70\% with a minimum of 0.5 d/m of Am\textsuperscript{241} detectable. Thorium, uranium, protactinium, neptunium, radium, and bismuth do not interfere. Curium and the cerium group rare earths interfere.
INTRODUCTION

This procedure was developed to meet the need for a routine sensitive and reliable differential chemical analysis for the determination of Am\textsuperscript{241} in the presence of plutonium in urine. There existed no americium urinalysis which met the above requirements.

The existing potential for simultaneous exposure to these nuclides in a plant handling aged plutonium emphasizes the need for the quantitation of metabolized Am\textsuperscript{241} in urine free from plutonium and uranium interference. The data obtained from routine urinalysis may be used for evaluation of possible low level exposures, estimation of Am\textsuperscript{241} body burden\textsuperscript{(1)}, and as an effective guide for medical therapy. The handbook value for a maximum permissible body burden of Am\textsuperscript{241} is 0.05μc (bone)\textsuperscript{(2)}.

The chemical method described in this paper ultimately yields a thin sample which can be counted without appreciable absorption of the alpha particles by solid materials and is free of other important alpha emitters.

Procedures have been reported for americium urinalyses\textsuperscript{(3,4)}. However, thorium and plutonium are carried through these processes. Other workers report very good separations of americium and plutonium by extraction of plutonium(IV) cupferrate into chloroform\textsuperscript{(5,6)}. Results obtained at Rocky Flats from attempted adaptation of this technique to urinalysis were quite variable and exhibited a decontamination fac-
tor of insufficient magnitude at the ultramicro activity levels encountered in urinalysis. Chetham-Strode, Jr.\(^{(7)}\) has used 2-thenoyltrifluoroacetone (TTA) for simultaneous extraction of americium and plutonium followed by selective stripping of americium from the TTA with 0.5 M nitric acid. However, the requisite pH of 4.8 for initial extraction is difficult to maintain, even with buffers, and quite often leads to the formation of emulsions in many systems. A variation of this technique was attempted. TTA was used to remove plutonium preferentially from a solution 1 M in nitric acid (optimum acidity). Satisfactory plutonium decontamination was achieved but americium recoveries averaged only 25–40%. Horner and Coleman\(^{(8)}\) conducted an extensive investigation of plutonium extraction from acid nitrate solutions by amines and organophosphorous compounds. Di(2-ethylhexyl)phosphoric acid (D2EHPA) was found to extract plutonium(IV) much more strongly than either amines or phosphine oxides. In one instance, the extraction coefficient (Ea) for americium was in the neighborhood of 10\(^{-3}\) as compared to approximately 10\(^4\) for plutonium.

This study suggested that an effective radiochemical separation procedure for americium from plutonium in urine could be devised through use of this reagent.
DISCUSSION

Principle of Method

The extraction mechanism\(^{(8)}\) appears to be extraction of a simple cation or cationic complex arising from plutonium-hydrogen cation exchange. The order of extractability is Pu(IV) > Pu(VI) > Pu(III).

Variables such as hydrogen ion concentration, extraction rate, concentration of sample constituents, D2EHPA concentration, and choice of organic solvent could be expected to affect markedly the distribution coefficient obtained in a solvent extraction of Pu with D2EHPA. These parameters were examined to determine conditions for the extraction which would insure quantitative removal of plutonium in a urinalysis procedure.

EXPERIMENTAL

Purification of Plutonium Stock

Alpha pulse-height analysis of the Pu\(^{239}\) stock solution used in this study revealed that approximately 8% of the total alpha activity was due to Am\(^{241}\). Measurement of high plutonium extraction coefficients and decontamination factors for this process would be severely affected by contamination of plutonium with even very small amounts of the poorly extractable americium. Therefore, the americium was effectively eliminated by extraction of the plutonium from 1 M HNO\(_3\) with 0.1 M D2EHPA + 0.1 M TOPO (tri-n-octylphosphine oxide) in Gulf BT. The extracted plutonium was scrubbed twice with 1 M HNO\(_3\) and stripped twice with 1 M Na\(_2\)CO\(_3\). The combined strip solutions were then acidified to give a stock solution
which was 1 M in HNO₃, and 1 M in NaNO₃. Am³⁴¹ activity in this purified solution was too low for detection by alpha pulse-height analysis.

Choice of Solvent

Chloroform was the solvent of choice since it possessed the desirable properties of density, non-flammability, miscibility with D₂EHPA, and low cost. Preliminary experiments also indicated satisfactory extraction of plutonium(IV) with D₂EHPA from nitric acid into solvent. The higher density of this solvent is a desired feature since it permits successive extractions of a single aqueous portion with the complexing agent.

Hydrogen Ion Concentration

Previous studies⁸ have shown that, as expected on the basis of the previously suggested reaction mechanism, extraction coefficients for plutonium(IV) decrease with increasing acidity over most of the nitric acid concentration range. However, these investigations were carried out in a kerosene-type diluent (Amsco 125-82). Therefore, similar studies in chloroform were conducted in order to ascertain the most favorable conditions for its use (Figure 1). Sodium nitrate had little effect as a salting agent on the extraction except at nitric acid concentrations less than 0.5 M.

Extraction Rate of Plutonium(IV) with D₂EHPA

The extraction rate was studied by preparing an aqueous solution of 2 M nitric acid containing a known tracer con-
Plutonium(IV) Extraction by D2EHPA:
Effect of Nitric Acid Concentration

\[
\begin{align*}
\Delta &= 0.01 \text{ M D2EHPA} \\
\Delta &= 0.05 \text{ M D2EHPA} \\
\Delta &= 0.1 \text{ M D2EHPA} \\
\text{Chloroform diluent}
\end{align*}
\]

**FIGURE 1**
centration of plutonium(IV) and extracting aliquots of this solution for different lengths of time with a solution of D2EHPA-chloroform. Phase ratios were aqueous/organic = 2:1. The extractions were carried out in separatory funnels, and a mechanical shaker provided good mixing of the phases.

It was observed that the extraction rates for both 0.05 M and 0.1 M D2EHPA in chloroform were extremely high and that extraction was quantitative within 2 - 3 minutes.

RESULTS

This procedure was investigated using urine collected from nonexposed personnel for spikes, control samples, and blanks. Since 1200 ml is considered as an average single-day void at Rocky Flats, mixed urine samples were divided into portions of this volume for experimentation. Spike samples consisted of pure americium and plutonium in known ratios while controls were urine samples to which either pure americium or pure plutonium were added at an activity level corresponding to its respective value in the matching spike sample. A blank was carried with each set of spikes and controls.

The americium or plutonium on the resultant sample planchet was determined by alpha counting. Plutonium decontamination was based on comparison of the alpha counts found on the control planchet with plutonium originally added to the control sample. A sensitive test for completeness of plutonium removal was made by alpha analysis of spike planchets with the Model H-100(9) alpha energy analyzer. (Figures 2 and 3).
FIGURE 2

Pulse-Height Analysis of Pu$^{239}$, Am$^{241}$ Spike Solution
Am$^{241}$ Activity: 5.28 ± 0.69 d/m
Pu$^{239}$ Activity: 1020 ± 30 d/m
Counted 15 minutes

FIGURE 3

Pulse-Height Analysis Showing Pure Am$^{241}$ Remaining in Spike
After Extraction of Pu with D2EHPA
Counted 16 hours
With this instrument, about 2% of plutonium alphas can be determined in the presence of americium. In every case, the americium was free of plutonium. Recovery of americium in the aqueous layer after extraction is shown in Table 1.

PROCEDURE

Reagents

Bromthymol Blue Indicator Solution -
Dissolve one gram of reagent grade indicator in 500 ml of distilled water made alkaline with one pellet of sodium hydroxide.

Bismuth Nitrate Solution -
Dissolve 231.2 g of bismuth nitrate [Bi(NO₃)₃ • 5H₂O-AR] in 660 ml of concentrated HNO₃ and dilute to one liter with distilled water. This solution contains 0.1 g of bismuth per milliliter.

4 N HCl -
Add 344 ml of concentrated hydrochloric acid to approximately 500 ml of distilled water in a volumetric flask and make up to one liter with distilled water.

6 N HCl -
Dilute 510 ml of concentrated hydrochloric acid to one liter in a volumetric flask.

8 N HCl -
Dilute 688 ml of concentrated hydrochloric acid to one liter in a volumetric flask.

- 72 -
<table>
<thead>
<tr>
<th>Sample</th>
<th>No. of Samples</th>
<th>Activity Added (g/m/1.2 liter)</th>
<th>Counting Time (min.)</th>
<th>Mean Alpha Activity Recovered (g/m)</th>
<th>Mean Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am-Pu</td>
<td>2</td>
<td>1200 ± 32</td>
<td>1020 ± 30</td>
<td>9</td>
<td>967 ± 26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80.6 ± 3.41</td>
</tr>
<tr>
<td>Am control</td>
<td>2</td>
<td>1200 ± 32</td>
<td>--</td>
<td>9</td>
<td>935.3 ± 28</td>
</tr>
<tr>
<td>Pu control</td>
<td>2</td>
<td>--</td>
<td>1020 ± 30</td>
<td>100</td>
<td>Background</td>
</tr>
<tr>
<td>Am-Pu</td>
<td>3</td>
<td>560 ± 17</td>
<td>1020 ± 30</td>
<td>15</td>
<td>432 ± 15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>77.1 ± 4.1</td>
</tr>
<tr>
<td>Am</td>
<td>3</td>
<td>560 ± 17</td>
<td>--</td>
<td>15</td>
<td>405 ± 14</td>
</tr>
<tr>
<td>Pu</td>
<td>3</td>
<td>--</td>
<td>1020 ± 30</td>
<td>150</td>
<td>Background</td>
</tr>
<tr>
<td>Am-Pu</td>
<td>10</td>
<td>5.28 ± 0.69</td>
<td>1020 ± 30</td>
<td>90</td>
<td>3.71 ± 0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70.2 ± 15.3</td>
</tr>
<tr>
<td>Am</td>
<td>10</td>
<td>5.28 ± 0.69</td>
<td>--</td>
<td>90</td>
<td>3.90 ± 0.57</td>
</tr>
<tr>
<td>Pu</td>
<td>10</td>
<td>--</td>
<td>1020 ± 30</td>
<td>150</td>
<td>Background</td>
</tr>
<tr>
<td>Am-Pu</td>
<td>7</td>
<td>0.74 ± 0.10</td>
<td>1020 ± 30</td>
<td>150</td>
<td>0.48 ± 0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>64.3 ± 25.6</td>
</tr>
<tr>
<td>Am</td>
<td>7</td>
<td>0.74 ± 0.10</td>
<td>--</td>
<td>150</td>
<td>0.42 ± 0.16</td>
</tr>
<tr>
<td>Pu</td>
<td>7</td>
<td>--</td>
<td>1020 ± 30</td>
<td>150</td>
<td>Background</td>
</tr>
</tbody>
</table>

* Corrected for background and blank values at 95% confidence interval.
Lanthanum Nitrate Solution

La(NO₃)₃, as received from the Lindsey Chemical Company, West Chicago, Illinois, is freed from actinium alpha emitting impurities on a Dowex-50X12 cation exchange resin column by the method of Farabee (10). The lanthanum nitrate stock solution obtained is used to prepare working solutions containing 25 mg of La⁺³/ml. Only solutions containing 0.05 d/m or less of alpha activity per mg of La⁺³ are used.

2M Hydroxylamine Hydrochloride -
Dissolve 139.0 g of C.P. grade hydroxylamine hydrochloride and dilute to one liter. Store in brown bottle.

2N Sodium Nitrite Solution
Dissolve 13.8 g of sodium nitrite (NaNO₂-AR) in distilled water in a 100-ml volumetric flask and make to volume with distilled water. Prepare fresh before use.

0.1M D2EHPA -
Add 32.3 g of di(2-ethylhexyl)phosphoric acid (Union Carbide Chemical Company) to chloroform-AR in a 1-liter volumetric flask and make to volume with chloroform.

8N KOH -
Dissolve 65.3 g of potassium hydroxide (KOH 86%-AR) in distilled water and dilute to one liter.

All other chemicals are either of reagent or C.P. quality.

Sample Pretreatment

The volume of a "24-hr equivalent" urine sample (two morning and two evening voidings) is measured and the sample transferred to a 2-liter beaker. The volume and the liquid level
are denoted on the beaker with a china-marking pencil or marking pen. Several glass beads, one ml of octyl alcohol and 200 ml of concentrated nitric acid are added. The beaker is covered with a Speede-Vap and placed over an asbestos pad on a hot plate at high heat. The sample is digested by gentle boiling until it attains a clear appearance.

BiPO₄ Coprecipitation

A stirring bar is added to the cooled solution and rapid stirring initiated over a magnetic stirring motor. Approximately 130 ml of concentrated ammonium hydroxide are added cautiously, followed by one ml of bromthymol blue indicator solution. Neutralization is completed by addition of concentrated ammonium hydroxide to the yellow-green endpoint. If necessary, the sample volume is readjusted to its original value with distilled water. Concentrated nitric acid is added to make the solution 0.15 M in HNO₃ (Table 2). 500 mg of hydroxylamine hydrochloride are added to the solution and the beaker placed in a steam bath heated to 80 ± 5 C. Concentrated phosphoric acid is then added to a concentration of approximately 0.09 M (Table 2). An amount of bismuth nitrate solution, equivalent to 60 mg bismuth per 100 ml, is added dropwise to the heated, stirred solution.

The precipitate is digested by an additional hour of stirring at 80 ± 5 C. The sample beaker is removed from the water bath and allowed to stand undisturbed for a minimum of three hours. The supernatant solution is carefully aspirated off (avoid disturbing precipitate) and the precipitate trans-
### TABLE 2

Solution Requirements for BiPO₄ Precipitation

<table>
<thead>
<tr>
<th>Urine Volume (ml)</th>
<th>Conc. HNO₃ for 0.15 M (ml)</th>
<th>H₃PO₄ (ml)</th>
<th>Bi(NO₃)₃ soln. (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>4.8</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>600</td>
<td>5.9</td>
<td>3.6</td>
<td>3.6</td>
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<td>700</td>
<td>6.8</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>800</td>
<td>7.5</td>
<td>4.8</td>
<td>4.8</td>
</tr>
<tr>
<td>900</td>
<td>8.7</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>1000</td>
<td>9.6</td>
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<tr>
<td>1100</td>
<td>10.5</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>1200</td>
<td>11.6</td>
<td>7.2</td>
<td>7.2</td>
</tr>
<tr>
<td>1300</td>
<td>12.45</td>
<td>7.8</td>
<td>7.8</td>
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<tr>
<td>1400</td>
<td>13.50</td>
<td>8.4</td>
<td>8.4</td>
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<td>1500</td>
<td>14.4</td>
<td>9.0</td>
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<td>1600</td>
<td>15.0</td>
<td>9.6</td>
<td>9.6</td>
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<tr>
<td>1700</td>
<td>16.4</td>
<td>10.2</td>
<td>10.2</td>
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<tr>
<td>1800</td>
<td>17.3</td>
<td>10.8</td>
<td>10.8</td>
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<tr>
<td>1900</td>
<td>18.5</td>
<td>11.4</td>
<td>11.4</td>
</tr>
<tr>
<td>2000</td>
<td>19.2</td>
<td>12.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>
ferred to a 90-ml Pyrex centrifuge tube with a distilled water rinse. The precipitate is centrifuged for 5 minutes at 2000 rpm and the supernate carefully discarded. The sample beaker walls are then rinsed down with 4N HCl from a wash bottle and the rinse transferred to the 90-ml tube. The final volume in the tube should be approximately 50 ml.

Wet-ashing of Bismuth Phosphate
Several drops of octyl alcohol are added to the HCl solution in the 90-ml tube; it is placed in an aluminum block at approximately 100 C and the solution taken to dryness. The dried sample is then repeatedly wet-ashed with several drops of concentrated nitric acid in a block heated to 350 C. After the sample has ashed to whiteness, it is evaporated twice with 8N HCl.

Lanthanum Fluoride Coprecipitation
The bismuth chloride ash is dissolved in 8 ml of 8N HCl and the solution is transferred to a 25-ml conical centrifuge tube. The walls of the 90-ml tube are rinsed with an additional 2 ml of 4N HCl and the rinse added to the centrifuge cone. After addition of 0.1 ml of La(NO₃)₃ solution, the tube contents are mixed thoroughly. Two ml of concentrated hydrofluoric acid (27M) are then added, and the solution stirred with a platinum stirrer. The tube is allowed to stand for 5 minutes and then centrifuged at 2000 rpm for 3 minutes. The supernatant is carefully aspirated and the precipitate dissolved in 2 ml of concentrated HCl.
Following the addition of 2 ml of distilled water, LaF$_3$ is reprecipitated by addition of 2 ml of 27 M HF. The preceding digestion and centrifugation steps are repeated. Five ml of 8N potassium hydroxide are added to the precipitate and carefully heated to boiling. After cooling, the mixture is centrifuged for 3 minutes and the supernate carefully drawn off.

**D2EHPA Extraction**

Following solution of the precipitate in 6 ml of 2 N HNO$_3$, one ml of 2M hydroxylamine hydrochloride is added, and the sample heated in a water bath at 70 C for 5 minutes. The tube is then removed from the water bath and 2 ml of 2M sodium nitrite solution are added with swirling. When bubble evolution ceases, the solution is transferred to a 30-ml separatory funnel. The centrifuge tube is rinsed once with 3 ml of 2N nitric acid and the rinse added to the separatory funnel. The aqueous layer is then extracted thrice with 5-ml portions of 0.1 M D2EHPA in chloroform for 5 minute periods. The chloroform extracts are removed and the aqueous layer is shaken for 3 minutes with a 5-ml portion of toluene. The aqueous portion is then withdrawn through the funnel stem into another 25-ml conical centrifuge tube. Lanthanum fluoride is precipitated by addition of 2 ml of 27M HF. The solution is allowed to stand 5 minutes, centrifuged at 2000 rpm for 3 minutes and the supernatant drawn off and discarded. Shake the precipitate with 10-15 ml of 1:100 hydrofluoric acid wash solution and centrifuge at 2000 rpm for 5 minutes.
Sample Planchetting
Aspirate the supernatant and invert the centrifuge cone quickly over absorbent tissue. Drain 15 minutes. Slurry the precipitate with distilled water and transfer to a stainless steel planchet with a disposable capillary pipette. Dry the disc under an infrared lamp and flame the dried planchet to red heat. The alpha activity is then counted with a low-background proportional counter for 150 minutes.

SUMMARY AND CONCLUSIONS
The analysis requires a maximum of two working days from the time a sample is received until the result is available. Refinements in the procedure resulting in an increased sensitivity would allow use of a smaller sample with accompanying decrease in sample collection time. In view of the large number of manipulations required in the procedure, differential analysis of a urine sample by means of an alpha energy analyzer would provide results requiring a minimum of elapsed time. However, the instrument time required for the pulse-height method in the case of low activity samples would disallow the possibility of conducting a differential analysis by this means on a routine basis. Hence, a differential chemical analysis of this type provides results in a relatively short period of time.
BIBLIOGRAPHY


DETERMINATION OF PLUTONIUM IN BIOLOGICAL SAMPLES

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Rochester, New York

The analysis of plutonium in dogs exposed to an aerosol containing the element required special treatment for some of the samples. The final estimation was made through the liquid scintillation counting technique and a separation scheme was necessary to isolate the element. The separation scheme itself was very simple and consisted of the absorption of a chloride complex of plutonium on an anion exchange column with subsequent elution. For certain samples the problem of getting the plutonium in a soluble form suitable for absorption by the resin was the most difficult.
INTRODUCTION

The analysis of plutonium in biological samples presents the investigator with the problem of analyzing low levels of the element in large and non-uniform samples. Plutonium-239 is an alpha emitter with a short range and a long half life. It can be ingested or inhaled. In our particular work at the University of Rochester, a team of investigators is interested in the fate and effects of plutonium administered as an aerosol to dogs by inhalation. The initial phase of the work required the analysis of the entire animal and its excreta. We were asked to devise an analytical procedure with particular emphasis put on the recovery of plutonium from lungs and the feces. Because the plutonium was administered as an aerosol through inhalation, the plutonium would be expected to concentrate in the lungs initially. However, the dog coughs up a good share of this, swallows it, and this part is largely excreted via the feces.

Preliminary studies using the Koshland method (a double precipitation and extraction) revealed two difficulties besides its cumbersome nature.

First: The separation scheme was far from complete for some samples, and relatively unsatisfactory for others (80% with wide limits at best). In particular, the recovery for fecal samples was extremely poor, less than 5%.

Second: The counting procedure which consisted of evaporating a small aliquot of the final TTA extraction on a planchet, firing the planchet to remove the organic matter, and then counting, was not exactly ideal. The firing step rendered some of the material airborne, which raised the background of the counting room and the temperature of some of our colleagues. In addition, a complete separation of plutonium must be accomplished, or serious quenching due to the absorption on the planchet would result.
Our analytical procedure consists of these three parts:

1. The plutonium is collected on an anion exchange column from a solution of ashed material.
2. The plutonium retained on the column is eluted with sulfurous acid.
3. The eluted sample is counted in a Liquid Scintillation Counter.

SPECIAL TREATMENT OF FECAL SAMPLES

The biggest problem lay in the first step, that of solution of some samples. An ashed fecal sample contains appreciable quantities of insoluble precipitate which trapped about 97% of the plutonium activity so that only about 3% would be measured in the usual scheme. Because of the importance of the fecal sample analysis in our studies we had to resort to some rather drastic procedures to effect the complete solution of this highly insoluble ash.

The original ash is treated with acid, and the acid portion is saved as the original acid soluble fraction. The insoluble ash is subjected to the treatment outlined in the following manner.

Treatment of Fecal and Insoluble Ashes

1. Treat insoluble portion with hydrofluoric acid and some sulfuric acid to remove silica.
2. Make a carbonate fusion of the dried residue.
3. Extract the carbonate fusion with water first and then hydrochloric acid but keep the two extractions separate.
4. Make a sodium bisulfate fusion of any insoluble residue from (3).

After the fusions, three separate fractions—(2) water soluble carbonate fusion, (3) acid soluble carbonate fusion and (4) bisulfate fusion—are obtained. The parts must be kept separate, but each is soluble in acid, and the plutonium in each part is separated by passage through an ion exchange column.
The distribution of plutonium in fecal ash subjected to this treatment is the following.

### Distribution of Plutonium in Fecal Ash

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Per Cent of Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
</tr>
<tr>
<td>2N HNO₃ extract</td>
<td>3.32</td>
</tr>
<tr>
<td>Water extract of carbonate fusion</td>
<td>14.4</td>
</tr>
<tr>
<td>HCl extract of carbonate fusion</td>
<td>80.5</td>
</tr>
<tr>
<td>Bisulfate fusion of residue</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Because most of the insoluble ash is CaSO₄, we were interested to see if CaSO₄ precipitated from an acid solution of plutonium would behave similarly. The analysis of such a CaSO₄ precipitate after the previous fusion treatment yielded the following distribution of plutonium.

### Distribution of Plutonium in Calcium Sulfate

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Per Cent of Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
</tr>
<tr>
<td>8N HCl extract</td>
<td>17.5</td>
</tr>
<tr>
<td>Water extract of carbonate fusion</td>
<td>5.6</td>
</tr>
<tr>
<td>HCl extract of carbonate fusion</td>
<td>75.5</td>
</tr>
<tr>
<td>Bisulfate fusion of residue</td>
<td>1.8</td>
</tr>
</tbody>
</table>

It is of interest to note that the bulk of the plutonium activity is in the acid soluble carbonate fusion part again. It is of equal importance to note that a precipitate formed in acid medium carries the plutonium with it. Therefore, it is imperative that all precipitation be prevented, which is the reason each part of the fusion is kept separate.

This procedure was necessary only for fecal and food samples. All other samples (urine, bone, soft tissues) are readily soluble in strong HCl.
SEPARATION

The separation scheme is simplicity itself. It is based on the studies of Wish and Rowell who studied the uptake of several actinides by an anion exchange resin from various acid solutions. In this batch process, the distribution of Pu as well as Np and U in strong HCl solutions is highly in favor of the resin. In terms of a column (which is essentially a large number of batch equilibrations carried out consecutively) such a distribution should mean complete pickup in a relatively short path.

In most extraction procedures (TTA, TBP, AA) the presence of phosphate constitutes a serious interference and requires a separation (the LaF collection step of Koshland). In a strong HCl solution non-dissociated phosphoric acid is formed and passes right through the column.

The greatest advantage in the use of the ion exchange column is that both the collection and separation are combined in one step. For the insoluble samples such as fecal ash, the ion exchange column provides a simple means of "reuniting" the four separate parts of the fused sample. Each part is passed through the column, and the entire sample can then be eluted. Samples low in activity can be concentrated on the resin.

The outlines of the separation scheme follows:

**Procedure for Separating and Counting Plutonium**

1. Dissolve sample in strong hydrochloric acid (100 ml 8N HCl and 2 ml conc. HNO₃).
2. Pass the solution through an anion exchange column to absorb the plutonium.
3. Elute plutonium from column with a saturated sulfurous acid solution.
4. Evaporate sulfurous acid solution to dryness, add 1 ml 3M phosphoric acid and proper amount of scintillating fluid, and count in a liquid scintillator.
Plutonium is absorbed on an anion column in the tetravalent state as a chloro complex of the form \(\text{Pu}({\text{Cl}}_6)^{-2}\). Nitric acid keeps the plutonium in the plus 4 state. Pu in the plus 3 state does not form a chloro complex.

Elution with \(\text{H}_2\text{SO}_3\) results in a double action on the Pu-chloro complex, first the destruction of the complex by the reduction of the Pu, and second the lowering of the chloride concentration. \(\text{H}_2\text{SO}_3\) is a very clean eluter, since evaporation removes the acid completely. After the traces of organic material from the resin are wet ashed, the sample can be prepared for counting.

We used Amberlite XE 117 anion exchange resin, 50-100 mesh. This is the same as the commercial Amberlite IRA 400 resin. The amount of resin used varied with the tissue, and generally those tissues with an appreciable concentration of iron need a longer column.

COUNTING

Let us now consider the problem of counting.

Two immediate advantages of liquid scintillation counting over the planchet method are (1) higher efficiency, and (2) the option of using an aliquot or the whole sample. A third advantage which we established was the tolerance for certain amounts of extraneous ions, which enabled simplification of the separation scheme.

The sample is prepared for counting by dissolving the ashed elution from the ion exchange column in phosphoric acid. Alcohol and phosphor solution are added, the solution cooled and then counted.

It is possible to count under plateau conditions, as is seen in the two graphs (Figures 1 and 2).
FIGURE 1

FIGURE 2
HCIO₄ QUENCHING

At first we dissolved our sample in perchloric acid because of its noncomplexing properties, but the counts decreased in time and adsorption onto the glass vial was suspected. To check this, the contents of one of the vials that had lost counts was discarded and the vial rinsed out with alcohol. Fresh acid, alcohol, and phosphor was added. The results showed a definite adsorption from the perchloric acid solution.

Adsorption of Plutonium from Phosphor Solutions Containing Perchloric Acid

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1st Treatment</th>
<th>2nd Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.0</td>
<td>6.8</td>
</tr>
<tr>
<td>2</td>
<td>15.9</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Because plutonium exists in the plus ⁴ state in perchloric acid, the obvious method for reduction of absorption would be that of reducing the positive charge. Known complexors such as EDTA, HCl, sulfuric acid, and phosphoric acid all gave steady counts for a pure plutonium sample. There was no loss of counts overnight. However, when iron was added, quenching resulted in the EDTA and HCl solutions, both of which were colored. Since iron accompanies Pu on and off the ion exchange column, and since iron is present in most biological samples, this is a serious disadvantage. This problem was solved by dissolving the sample in phosphoric acid. Iron forms a colorless complex with phosphoric acid and up to 1 mg. of iron may be tolerated in our counting procedure.
RECOVERY

The recovery of plutonium added to tissues, ashed, and separated by ion exchange technique follows; the fecal and food samples have been fused to make the precipitate soluble.

Recovery from Spiked Samples

<table>
<thead>
<tr>
<th>Type</th>
<th>% Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feces B</td>
<td>101</td>
</tr>
<tr>
<td>L</td>
<td>100.6</td>
</tr>
<tr>
<td>Food J</td>
<td>95.7</td>
</tr>
<tr>
<td>019</td>
<td>99.9</td>
</tr>
<tr>
<td>Urine C</td>
<td>101</td>
</tr>
<tr>
<td>D</td>
<td>93</td>
</tr>
<tr>
<td>K</td>
<td>101</td>
</tr>
<tr>
<td>L</td>
<td>99.9</td>
</tr>
<tr>
<td>Bone VII</td>
<td>96</td>
</tr>
<tr>
<td>VIII</td>
<td>94</td>
</tr>
<tr>
<td>IX</td>
<td>96</td>
</tr>
<tr>
<td>Liver XIX</td>
<td>96.2</td>
</tr>
<tr>
<td>XXI</td>
<td>98.4</td>
</tr>
<tr>
<td>Spleen IV</td>
<td>96.0</td>
</tr>
<tr>
<td>VI</td>
<td>97.6</td>
</tr>
<tr>
<td>VIII</td>
<td>98.2</td>
</tr>
</tbody>
</table>

DISCUSSION

For the conditions for which this procedure was designed, that is, the analysis of the plutonium content of dog tissues and excreta after exposure to a plutonium aerosol, the separation is complete. However, it is known that several other ions (Np and U) also form a strong complex which is adsorbed on the anion exchange resin. It was of interest to determine what activity would be found by our method in the tissues and excreta of a dog of unknown history, but of no known plutonium exposure. We were particularly interested in the activity in the lungs. The results of the analysis of the "blank dog" show that the only significant counts were in the thigh bone.
Activity in an Unexposed Dog

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight, g</th>
<th>Net cpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lung lobe A</td>
<td>5.0</td>
<td>13</td>
</tr>
<tr>
<td>B</td>
<td>8.5</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>14.7</td>
<td>16</td>
</tr>
<tr>
<td>Bone: Rib</td>
<td>43.3</td>
<td>8</td>
</tr>
<tr>
<td>Thigh</td>
<td>141.5</td>
<td>48</td>
</tr>
<tr>
<td>Skin</td>
<td>155</td>
<td>13</td>
</tr>
<tr>
<td>Liver</td>
<td>106.3</td>
<td>12</td>
</tr>
<tr>
<td>Urine 12 hour</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Fecal 12 hour</td>
<td>36</td>
<td></td>
</tr>
</tbody>
</table>

Background: 70-80 cpm.

On the basis of 1 microgram of cold uranium counting 1 cpm, we estimate that 1 g thigh bone contains about 0.34 microgram of cold uranium. This figure is higher than the accepted norm, but due to the sketchy history of this dog, we will not speculate further on the natural radioactivity of the "blank dog". Of special interest to us is the low activity in the lungs where the primary interest of our colleagues lies.

In summary, we have devised a simple separation scheme in conjunction with a liquid scintillation technique which is suitable for the plutonium measurement of biological samples.
A DEVICE FOR MEASURING THORON IN THE BREATH

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An instrument has been developed to measure the gas thoron. The gas is adsorbed on charcoal and the alpha particles from Em$^{220}$ and from Po$^{216}$ arrive with 2$\pi$ geometry at a ZnS powdered lucite screen viewed by a 1/4 inch photomultiplier tube.

By deemanation of solutions prepared using known amounts of aged thorium chloride it has been found that a sample count equivalent to background of the system is obtained with a solution containing $1 \times 10^{-11}$ curies of Ra$^{224}$.

Measurements have been made on two thorotrast patients and for these subjects it appears that about 13 - 14 percent of the thoron produced is given off in the breath.
INTRODUCTION

Thoron is a gaseous 54.5 sec. half life daughter in the thorium series. A fraction of the thoron formed in individuals with a thorium body burden is expired in the breath. Thoron in the breath has been measured by a variety of detection devices. Aub, Evans, Hempelmann, and Martland (1952) collected the 10.6 hour half life ThB (Pb$^{212+}$) by electrostatic deposition on a disc centrally located in a 12-liter breath hold-up tank. Alpha counts were made of the Po$^{212+}$ daughter, once removed from ThB. To achieve high sensitivity, the subject must breathe into the apparatus for several hours. Rundo (1958) collected the subject's breath in a plastic bag for 30 seconds, then transferred it rapidly into a previously evacuated 4-liter ionization chamber, and counted thoron and ThA (Po$^{216+}$) as they decayed with approximately the 54.5 sec. half life of thoron. Zimmerman and Bouvier (1955) developed a method of thoron measurement in order to estimate the thorium content of ores. The ore was dissolved and the solution was swept by air which then passed by concentrically arranged lucite-cylinder-supported ZnS coatings. At one end of this array a photomultiplier detected the light pulses piped by the lucite.

DESCRIPTION OF THORON DETECTOR

The detection system for breath thoron to be described below uses scintillation detection like the Zimmerman-Bouvier device, but, unlike it, retains thoron in the sensitive volume of the detector rather than measuring it en passant. In this device the thoron is adsorbed on finely granulated...
activated charcoal in close proximity to a ZnS-coated lucite screen viewed by a photomultiplier tube. Figure 1 shows the construction of the detector. When assembled the ZnS-coated lucite disc rests on a ledge just above the gas outlet holes and, sealed in with a light application of silicone stopcock lubricant, forms the upper boundary of an air chamber about 0.32 cm. deep and 13.4 cm. in diameter. The thoron-containing gas enters the chamber through the central 0.63 diameter hole and escapes through a series of 1 mm. diameter holes equally spaced around the periphery into a manifold which is vented through the outlet tube seen at the bottom of the illustration. The charcoal surface is prepared by coating an 11.5 cm. diameter aluminum 0.16 cm. thick disc with a layer of pressure-sensitive adhesive* and dusting on activated charcoal particles** 250 x 300 mesh size. This disc is then placed on the face of a copper plate to which the cooling fins have been soldered. In operation the cooling fins are immersed in an alcohol-solid-CO₂ mixture and the charcoal cooled to approximately -70° C. A teflon ring joins the cooled copper plate to the stainless steel manifold and acts as a heat conduction barrier. The phototube illustrated is a 5-inch diameter Dumont Photomultiplier, Type 6364.

THE MEASUREMENT SYSTEM

Figure 2 illustrates the measurement system. The subject is fitted with a valved mask. In the illustration he is breathing room air, but the capability of connecting to a tank of compressed air is available. The expired breath may be either passed in toto into the spirometer, marked (1),

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* Bostik Cement No. 4777-270 obtained from B. B. Chemical Co., Cambridge, Massachusetts.

** Screened from activated coconut charcoal particles supplied by Barnevbe^{-}Cheney Company, Columbus, Ohio.
Illustration of the thoron detector. The activated charcoal is 250 x 300 mesh dusted on a Bostik coated (pressure adhesive) aluminum disc. The ZnS coated lucite disc is held on the phototube face by silicone lubricant.
The measurement system: The various marked components are 1) a spirometer serving as a variable volume breath reservoir, 2) a smoked kymograph drum, 3) CO$_2$ and water vapor trap, 4) the thoron detector, 5) a gas meter of the bellows type, and 6) the columns containing the solutions of known thorium content.
or a measured fraction may be by-passed into a gas meter, marked (5), depending on the minute volume of the subject. A separate, central vent from the spirometer leads into a soda lime + drierite + magnesium perchlorate trap, marked (3), to remove CO₂ and water vapor, and thence to the detector. Approximately 2 cm. of water pressure above atmospheric is produced in the spirometer gas volume by a weight placed on top of the bell. This pressure serves to drive the gas through the trap and the detector at a constant rate. In usual operation the weight and by-pass aperture are adjusted so as to produce a flow rate of 4 to 5 liters per minute through the detector. In each case the expired air which has passed through the detector is collected in a large balloon for a measured length of time and the volume determined at the conclusion of the experiment. Since the decay of thoron en route from the mouth to the detector must be known with reasonable accuracy, the fixed air volume of the trap, the face mask, and the connecting tubes must be measured for a given apparatus, and the average air volume of the spirometer must be determined for each subject. The spirometer bell is raised during the subject's expiration and falls when the subject inspires room air. During the preliminary period while the subject is becoming accustomed to the breathing mask, the operator spills spirometer air into the gas meter so as to establish a recurrent minimum spirometer volume of about 100 ml. The volume change of the spirometer is recorded by a stylus attached to the bell marking on a revolving kymograph drum, designated as (2) in Figure 2. The record permits the estimate of an average volume for each run.

The thoron + ThA deposit grows rapidly, and the count per minute reaches a constant value within five minutes after the breathing period begins. The steady state count rate is read either from a scaler or registered on a
counting-rate-recorder system.

The necessary data are (1) the subject's ventilation rate, (2) the rate at which the breath is passed through the detector, (3) the effective average volume between the subject's mouth and the detector, and (4) the steady state counting rate. As will be shown later, these data enable a calculation of the partial pressure of thoron and therefore the activity released per unit time at the subject's mouth.

CALIBRATION OF THE SYSTEM

For calibration of the system, solutions of ThCl₄ were made up from a supply of salt which has aged at least 30 years from its time of preparation. The importance of this can be illustrated by citing the pertinent portion of the thorium decay chain. Th²³² (α, 1.39 × 10¹⁰ y) → Ra²²⁸ (β, 5.75 y) → Ac²²⁸ (β, 6.13 hr.) → Th²²⁸ (α, 1.9 y) → Ra²²⁴ (α, 3.64 d.) → Em²²⁰ (thoron α, 54.5 s) → Po²¹⁶ (α, 0.16 s) → Pb²¹² (β, 10.6 h). The rate of formation of thoron atoms is equal to the rate of decay of Ra²²⁴. In turn, this rate is readily arrived at if the weight of Th²³² and its half life are known and if the daughter products through Ra²²⁴ are in radioactive equilibrium. The limiting daughter in growth of the equilibrium state is Ra²²⁸ with a 5.75 year half life (May, Atherton, Lloyd, Lucas, Stover, and Bruenger, 1962). The assurance that the ThCl₄ has been aged at least 30 years establishes that Ra²²⁸ is present in at least 97 percent of radioactive equilibrium with Th²³². Three standard solutions were prepared containing respectively, 0.0265 g., 0.0796 g., and 0.143 g. of Th dissolved as the chloride salt in 75 ml. of 5% HCl. Each solution was transferred to a 250 ml. capacity bubbling tower, marked (6), in Figure 2. The tower is constructed with a medium porosity fritted disc to
break up the gas into small bubbles which sweep the solution.

Connections from the compressed air tank are provided so that the gas flow may be divided between the tower and a by-pass circuit in continuously adjustable fractions. The two paths join after passing through independent drierite + magnesium perchlorate water traps and go directly to the gas inlet of the detector. Flow through the bubbler and through the detector is indicated by Manostat flow meters with a range up to 18 liters per minute of air at standard pressure and 21° C. temperature. As a further check on total flow rate, the gas meter was connected to the detector gas outlet. For slow rates a correction was applied to the gas meter data because of the reduction in temperature of the gas during passage through the detector.

Preliminary experiments showed that the lowest rate of flow (0.8 lpm.) used in calibration removed all of the thoron formed in the solution. The distribution of thoron on the charcoal surface of the detector from the central inlet to the peripheral outlets is a continuous function of the changing thoron partial pressure and of residence time in the chamber. At any given rate of gas flow, it would be expected that the pattern of distribution of thoron would be the same and that the ratio of the entrant partial pressure of thoron to the exit partial pressure would be equal, independent of differences in thoron concentration in the gas. So long as decay during transit of the chamber is negligible, the thoron exit partial pressure should increase with gas flow rate. For flow rates of interest in the present application the above condition is fulfilled. Figure 3 illustrates the way in which the ratio of the exit partial pressure to the entrant partial pressure varies with flow rate. This graph was constructed from data obtained by experiments in which two similar detectors were placed in series.

Since, in the measurement of breath thoron, the flow rate through the
The ratio of exit thoron partial pressure divided by the entrant partial pressure as a function of flow rate through the detector.
detector will have an upper limit defined in the system described by the greatest spirometer weight which can be lifted without discomfort and a lower limit defined by total minute volume which in some individuals may be as low as 3 liters per minute, calibration must be made over a range of flow rates. The calibration procedure therefore consisted in using each of the three standard solutions, in turn, at flow rates ranging from 0.8 liters per minute to 10 liters per minute. Since the "dead space" volume is known and the flow rates through the tower and the by-pass gas channel are measured, the decay en route to the detector can be calculated. For each source and flow rate, an entrant partial pressure of thoron can be assigned. Typical calibration data are illustrated in Figure 4. The points fall quite nicely on the straight lines which would be expected for physical adsorption at very low gas pressures and constant temperature. These data and others like it are used to construct the working graph reproduced in Figure 5.

MEASUREMENT OF SUBJECTS

Two subjects with known thorotrast burdens were available for study. A first and second measurement at one-month intervals was made on each man. Although these subjects were elderly, they experienced no difficulty in breathing through the face mask and the operator was able to make adjustments so that a reasonably constant average spirometer volume was maintained for the measurement period. A standard was routinely run at the conclusion of the experiment to verify that the charcoal was adsorbing at its full capacity. The results are presented in Table I.

The output of thoron in the breath may be related to the body content of Ra$^{224}$ estimated at 0.082 µc for subject M and 0.094 µc for subject V. It may therefore be stated that 11 to 12 percent of the thoron formed per minute escapes in the breath of the subject. A greater number of subjects will be
The calibration data indicating steady state counts per minute as a function of thoron partial pressure at the gas inlet of the detector for each of the indicated gas flow rates.

The working calibration graph derived from data such as illustrated in Figure 4. If the flow rate through the detector is known, a constant may read from the graph to convert steady state counting rate to partial pressure of thoron at the detector inlet.
Table I

MEASUREMENTS OF BREATH THORON FROM TWO THOROTRAST PATIENTS

<table>
<thead>
<tr>
<th>Subject</th>
<th>M</th>
<th>M</th>
<th>V</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial number</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Ventilation rate in lpm</td>
<td>8.50</td>
<td>6.82</td>
<td>11.70</td>
<td>11.64</td>
</tr>
<tr>
<td>Rate through detector in lpm</td>
<td>5.10</td>
<td>3.85</td>
<td>4.25</td>
<td>5.37</td>
</tr>
<tr>
<td>Fixed system dead space in liters</td>
<td>0.951</td>
<td>0.951</td>
<td>0.951</td>
<td>0.951</td>
</tr>
<tr>
<td>Average spirometer volume in liters</td>
<td>0.341</td>
<td>0.485</td>
<td>0.660</td>
<td>0.322</td>
</tr>
<tr>
<td>Decay time in minutes</td>
<td>0.253</td>
<td>0.373</td>
<td>0.379</td>
<td>0.237</td>
</tr>
<tr>
<td>Decay factor</td>
<td>0.824</td>
<td>0.752</td>
<td>0.748</td>
<td>0.834</td>
</tr>
<tr>
<td>Net counting rate in cpm</td>
<td>5520</td>
<td>4870</td>
<td>3594</td>
<td>3966</td>
</tr>
<tr>
<td>Factor to convert thousands of counts per minute to entrant partial pressure of thoron</td>
<td>0.120</td>
<td>0.140</td>
<td>0.134</td>
<td>0.119</td>
</tr>
<tr>
<td>Partial thoron entrant pressure in units of $10^{-16}$ mm</td>
<td>0.6624</td>
<td>0.682</td>
<td>0.481</td>
<td>0.476</td>
</tr>
<tr>
<td>Partial thoron pressure at mouth in units of $10^{-16}$ mm</td>
<td>0.804</td>
<td>0.907</td>
<td>0.644</td>
<td>0.566</td>
</tr>
<tr>
<td>Microcurie thoron per minute in breath</td>
<td>0.0077</td>
<td>0.0069</td>
<td>0.0084</td>
<td>0.0075</td>
</tr>
</tbody>
</table>
measured to determine a more meaningful average.

**SOURCES OF ERROR**

1. **Contamination of Charcoal:** Water vapor must be reduced to very low pressure so that an absorptive layer of ice does not form. During early calibration runs, with Drierite alone as a water absorbent, a small steady reduction in counting rate occurred over several hours. The addition of magnesium perchlorate (reducing the water vapor to 0.002 mg. per liter air) solved this problem.

   Using a tank gas mixture simulating expired air (3.5% CO₂) to sweep the calibration towers, it was found that removal of the CO₂ trap caused only 10 percent reduction in the steady state thoron counting rate.

   Some organic gases, e.g. formaldehyde vapor, destroy the absorptive capacity of the charcoal for thoron very rapidly. On the other hand, if the train is kept free of water and unfavorable vapors, the same charcoal layer may be used repeatedly with no loss in sensitivity.

2. **The Measurement of Decay Time Between the Mouth and the Detector:**

   In general, the gas train volume associated with decay and the gas flow rate may be measured with sufficient accuracy. An error of 100 ml. in the estimation of volume, assuming a total of 1 liter dead space, for rates of 5 liters per minute through the detector produces an error of 1.5 percent in the decay factor used to convert entrant partial pressure of thoron to mouth partial pressure.

3. **Measurement of Subjects Ventilation Rate:** Any errors in the subject's ventilation rate are reflected directly in the final result. Mask-to-face connection must be tight so that no air is lost. Flow meters must be calibrated and gas should be measured at a known temperature so that necessary corrections may be made.
4. **Calibration of Thoron Partial Pressure per 1,000 Counts per Minute versus Counting Rate:** The calibration of the detector can be made quite precisely. For reasons indicated earlier the standard solutions must be prepared from old thorium salts or alternately from thorium salts in which the Th\(^{228}\) content is accurately known. A given calibration is applicable to the particular detector and the charcoal size used in preparation of the screen. Differences in detector design produce different flow patterns and may consequently produce different patterns of thoron adsorption. The charcoal particle size determines the available adsorption surface and also modifies the effective geometry of the detector because particle size is a factor in the absorption of alpha particles starting out at small angles relative to the planar surface.

5. **Corrections for Aggregation of Pb\(^{212}\) (ThB):** The thoron deposited on the active charcoal layer decays to the Po\(^{216}\) daughter which, because of its 0.16 second half time, comes rapidly into equilibrium and doubles the counting rate. Po\(^{216}\) decays, in turn, to Pb\(^{212}\) with a half time of 10.6 hours. The amount of the latter nuclide increases throughout the observation period. However, for breath thoron measurements at a counting rate 5,000 cpm. (approximately 6,600 dpm. of thoron in our system), a counting period of 15 minutes would yield a total of \(1 \times 10^5\) atoms of Pb\(^{212}\). Therefore, at the end of the period one might expect less than 41 counts per minute addition to background from this source. The contribution from Pb\(^{212}\) would therefore be less than 1 percent of the total counting rate, and thus negligible for the usual breathing periods involved in measurement of breath thoron by this method.

**EFFICIENCY AND SENSITIVITY OF THE DETECTOR**

At favorable flow rates, when substantially all of the thoron is
adsorbed, an effective geometry may be assigned. With the detector described above, a 250 x 300 mesh charcoal particle size, and a flow rate of 1.45 liters per minute the ratio of counts per minute from thoron to the calculated disintegrations per minute of thoron introduced at the detector gas inlet is 0.38. The failure to achieve $2\pi$ geometry is due 1) to the true geometrical relationship complicated by the unhomogeneous distribution of thoron on the charcoal covered plate, and 2) to the absorption by the charcoal particles of alphas starting off at small angles.

The sensitivity of the apparatus is such that 0.7 cpm, net may be obtained from 1.0 pc. of thoron gas per minute referred to the subject's mouth, with background equal to less than 0.2 cpm. For breath levels of 10 pc. per minute and a counting period of ten minutes, the standard deviation would be $\pm 12$ percent due to counting statistics.

In order to consider improvement of the present system, the factors which operate to cut down sensitivity may be identified and weighed. From 1 pc. per minute (at the mouth), the maximum $4\pi$ counting rate at the detector (thoron + P$_{214}$) would be 6.4 cpm, if no loss whatever occurred.

1. Part of the subjects expired breath is by-passed and never reaches the detector. The fraction going through the detector varies with the subject. In the examples cited in Table I, at best (M, 1) 60 percent went through the counting circuit and at worst 36 percent (V, 1). Using 56 percent (M, 2) as a readily obtainable distribution, the reduced expected count is $0.56 \times 6.4 = 3.59$ counts per minute. It is easily conceivable that by a variety of means the system might be made to accommodate the entire minute volume of the subject's expiration. By reference to Figures 4 and 5, it can be seen that with the present chamber dimensions an increased flow rate from, let us say, 5 to 10 liters per minute falls far short of
doubling the counting rate because of the higher exit partial pressure of thoron with the higher rate. Therefore, a significant reduction of this source of loss implies construction of a larger or more efficient surface for adsorption.

2. Decay en route to the detector (see Table I) reduces the counting rate to $0.75 \times 3.59 = 2.7$ cpm. For breathing periods limited to 20 minutes, smaller traps could be used or, alternately, a number of smaller traps could be prepared and a fresh trap from the stand-by capacity cut into the circuit as needed.

3. The effective geometry factor in this case combines true geometry with the experimentally unresolved absorption of alpha particles by charcoal granules. This factor, measured as 0.38, reduces the expectation to $0.38 \times 2.7 = 1.03$ cpm. This loss could be probably somewhat reduced by using 300 x 325 mesh charcoal granules instead of the 250 x 300 mesh used in the subject measurements cited in Table I. To achieve better than 2 % geometry implies radical redesign of the detector unit.

4. At rates of 3.85 liters per minute, $(M, 2)$ 32 percent of the thoron passes out through the detector gas outlet. This last source of loss reduces the expected count to $0.68 \times 1.03 = 0.7$ cpm. In order to reduce this loss, a more efficient adsorption design or a larger detector will be required.

OTHER APPLICATIONS OF THIS DEVICE

This system may be used to measure Th$^{228}$ in solutions. Under these circumstances, lower flow rates and smaller water vapor traps may be used. We have set up such an apparatus and prepared a standard containing 566 pc. of Th$^{228}$. The gas volume in the trap plus the volume over the solution in the bubbling tower was 165 ml. We chose this opportunity to explore the
effect of the size of charcoal granules. The results of different flow rates are presented in Figure 6.

The data show that reducing the granule size is effective in increasing the count. Using favorable particle size and flow rate, the device yields 1.6 cpm. per pc. Th$^{228}$. The background may be kept to 0.2 cpm. or less. Therefore, a 30-minute count of 1 pc. Th$^{228}$ would yield 54 counts with a standard deviation of about 7 to 9 counts. With counting times in excess of 30 minutes, we experienced some loading of the water vapor traps and reduction in counting rate, indicating the need for larger traps or more efficient trapping for longer periods.

SUMMARY

A device to adsorb and count thoron from the breath of human subjects has been described. In its present form it will measure thoron referred to the patient's mouth with a sensitivity of 0.7 cpm. per pico-curie of thoron per minute with a background of less than 0.2 cpm. If one assumes 10 lpm. ventilation rate, the system would detect thoron in concentrations of 0.1 pc. per liter breath. The minimum level for measurement in ten minutes is a breath output of 10 pc. per minute. It is also shown that, when used to measure Th$^{228}$ in solution, the device has a sensitivity of 1.6 counts per minute per pc. of Th$^{228}$.

ACKNOWLEDGMENT

We wish to acknowledge the excellent technical assistance of Mr. James Johnson and Mr. David Schiffman in carrying out preliminary phases of these experiments.
The steady state counting rate for the thoron from a solution containing 0.0053 grams of Th$^{232}$ is shown as a function of gas flow rate through the detector for activated charcoal preparations with three different ranges of particle size as indicated by the mesh gauges marked on the curves. The vertical lines associated with the points indicate the standard deviation due to counting error. The interpretation of these results is that alpha particles starting off at low angles are absorbed to a greater extent by large charcoal particles than by small.
REFERENCES


A procedure is discussed for electroplating alpha sources for use in calibrating alpha counting instruments. This procedure contains details for those interested in making secondary alpha standards for use in their respective operations. Economy and ease of supply are the motivating factors in making electroplated alpha sources for instrument calibration.

Compilation of electroplating results is shown for plutonium and for uranium.

Useful techniques are covered which add to the efficiency of the operation.
INTRODUCTION

Standard alpha sources play an important role in standardization of all alpha type instruments. Calibration of the instrument is the most important step in procuring statistically valid results. Standards that will remain constant in value over long periods of time are a necessity. The quality of the plating should dictate, to a great extent, the time that the standard source will remain constant.

The major portion of sources produced are plutonium 239 plated on a stainless steel disc.

DISCUSSION

Instrumentation

The power supply for electroplating consists of a high-current transformer and bridge rectifier capable of delivering 30 amps at 24 volts, safe margin. From this supply four anodes are connected through individual resistance potentiometers, ammeters and fuses. Each anode supply is monitored with a voltmeter. Figure 1 is a schematic drawing for this power supply.

FIGURE 1
Cell Design

A stainless steel base with a threaded Teflon top is used as the cell or standard holder. A ventilated Lucite cap is used to hold the platinum anode. This cap is adjustable so that the anode can be raised or lowered to maintain the proper current density. Figures 2 and 3 are photographs of the cell base, cell body and adjustable anode cap used for electroplating standards. Figure 4 is a drawing of the adjustable anode cap.

The disc becomes the cathode. A variety of materials can be used for source discs but No. 4 finish, #304 stainless steel is preferred at this facility for its ruggedness and quality plating. The anode is 20-gauge platinum wire formed into a spiral on one end, and is large enough to cover the plating area and maintain current density.

PROCEDURE

Sufficient plutonium nitrate solution is pipetted into the cell to yield a source of a desired value based on an average recovery of 85%. Add approximately 15 ml 1N potassium hydroxide to cover completely the spiral platinum electrode. Three ml of sodium hypochlorite is then added to oxidize the plutonium(IV) to plutonium(VI). The plutonyl ion is preferentially plated. The cell must be tilted to a 14° angle. The resultant convection currents circulate the solution for uniform heating. Heat, being a function of resistance in this case, maintains the temperature of the
solution to slightly below boiling. Should the solution begin to boil, a slight decrease in amperage will maintain a lower temperature in the cell. The voltage is adjusted to 15 volts by raising or lowering the anode to increase or decrease the resistance in the cell.

Under these conditions the time required to plate a standard source is approximately one hour. However, the time is inversely proportional to the current for a given amount of material. If the current is reduced to maintain a lower temperature, more time will be needed to complete the standard source. The time is also a function of the efficiency of the total electroplating system. Figure 5 demonstrates the inverse proportionality of the amperage versus time.

![Graph showing inverse proportionality of amperage versus time. Each point is an average of four samples.](image-url)
Experience will dictate time and current for different source preparations. The discs are then removed from the cell and counted in an alpha instrument to estimate the activity. If the activity is more than the required amount, it can be rapidly and easily removed.

To remove the activity, the disc is placed in the cell and 1N potassium hydroxide added to cover the platinum electrode. The leads are reversed so that the disc becomes the anode and the platinum spiral becomes the cathode. Setting the amperage and the voltage at the proper point, flipping the switch momentarily on, then off, will backplate a small amount of material from the disc to the platinum spiral electrode. Utilizing this technique effectively reduces the source count to the desired value.

When the desired count rate has been obtained, methyl alcohol can be used to clean the standard. After cleaning, it should be flamed(5). Figure 6 tabulates some typical electroplating results for plutonium. The average recovery of plutonium-electroplated standards is 85% but this will vary with the amount of material being electrodeposited on a given area.

This electroplating procedure can be used in preparation of discs for alpha pulse-height analysis. A thin sample is needed for good resolution in identifying unknown spectra(6).

Am\textsuperscript{241} growth occurring from beta decay of Pu\textsuperscript{241} increases the alpha activity after approximately two years. This growth after five years can change the geometry of an alpha

- 116 -
<table>
<thead>
<tr>
<th>Plate Type</th>
<th>Activity Type</th>
<th>Activity into cell, d/m</th>
<th>Voltage</th>
<th>Current (amp.)</th>
<th>Time (min)</th>
<th>Plating Standard</th>
<th>Value d/m</th>
<th>Percent Recovery</th>
<th>Percent Deviation</th>
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<td>90</td>
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<td>2.5</td>
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<td>60</td>
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<td>± 0.4</td>
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standard by as much as 11%\(^{(6)}\). The growth of Am\(^{241}\) as a function of time is shown on Figure 7. Each year the standards should be calibrated with a primary standard and assigned a new value.

**Uranium-Electroplated Standards**

The same equipment may be utilized for uranium source preparation as is used for plutonium electrodeposition. Saturated ammonium oxalate is the electrolyte used for uranium electrodeposition\(^{(3)}\). Current should be around 2.2 amp. and voltage should be 15 volts for rapid and efficient plating. This can be controlled by use of the adjustable anode cap. Rate of plating is dependent on the efficiency of the total unit. Normal and depleted uranium plate very similarly to enriched uranium. Figure 8 illustrates some typical results of enriched uranium electrodeposition.
### FIGURE 8

<table>
<thead>
<tr>
<th>Plate Type</th>
<th>Activity Type</th>
<th>Activity into cell, d/m</th>
<th>Voltage (amp.)</th>
<th>Current Time (min.)</th>
<th>Plate Value (μm), m</th>
<th>Diameter, Area (μm)</th>
<th>Percent Recovery</th>
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<td>11,300</td>
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</table>
CONCLUSION

Alpha sources, when used frequently as secondary standards, may be conveniently and rapidly prepared by an electroplating method. Techniques have been discussed which are used at Rocky Flats Division Health Physics department.

BIBLIOGRAPHY


(4) George W. Royster, Jr., "Electrodeposition of Uranium from Urine", Health Physics 2, 3 (1960).


DETERMINATION OF TOTAL RADIOSTRONTIUM IN BIOLOGICAL SAMPLES
IN THE PRESENCE OF LARGE QUANTITIES OF CALCIUM*

A. L. Boni
E. I. du Pont de Nemours and Co.
Savannah River Plant
Aiken, South Carolina

Improved recovery of total radiostrontium from biological samples containing large quantities of calcium has been attained through the use of potassium rhodizonate as a selective precipitating agent. An analytical procedure utilizing this method was developed, and optimum conditions for an 85% chemical recovery were determined.

* Published in:
The coincidence counter has been useful in determining the amounts of various radioactive nuclides present in routine samples. An application of this method in determining the amounts of Zr$^{95}$, Nb$^{95}$, Ru$^{103}$, and Ru$^{106}$ present in samples containing aged fission products will be described. The method does not require solids-free mounts or mounts made on thin films.

The equipment consists of beta and gamma probes, a fast single channel analyzer, and a multiple channel analyzer. A stilbene crystal is used for the beta detector and a sodium iodide crystal is the gamma detector. The fast single channel analyzer selects the energy band of pulses from one detector to trigger the coincidence circuit of the multiple channel analyzer. The pulses from the other detector are analyzed only if they are in coincidence with the pulses passing through the single channel analyzer. The energy calibration of the sodium iodide crystal is determined with Co$^{60}$, Cs$^{137}$, and Np$^{237}$-Pa$^{233}$. The calibration of the stilbene is determined with Cs$^{137}$, Sn$^{113}$, Np$^{237}$-Pa$^{233}$, and Ta$^{182}$.

The correction for the solids on the sample plate may be determined by a mathematical method combined with a counting method or with the response of the counter to an internal standard. Both methods require calibration curves, with each pure nuclide, of the energy distribution and intensity of the betas and gammas as a function of the amount of Nucl. Sci. and Eng., Vol. 14, 249-253 (1962)
solids on the plate. The attenuation of the internal standard coincidence counts is a function of the amount of solids on the plate. The attenuation of the other betas or coincidence counts can be determined from the known solids on the plate and the calibration curves for each nuclide. The mathematical method uses two of the known nuclides in the sample and compares the ratios of the coincidence counts to the gamma counts for two different beta energy bands. The ratios are a function of the amount of solids on the plate and the amount of solids can be calculated from the calibration curves. The choice of the method used must be based on the nuclides present and the availability of a suitable internal standard as well as the preference of the individual.
In February, 1961, a chemical operator at the Weldon Spring AEC Feed Materials Processing Plant operated by the Mallinckrodt Chemical Works was accidentally burned by a molten solution of uranyl nitrate. The employee was hospitalized for treatment of second degree burns. Samples were immediately collected for bio-assay as well as for routine clinical investigation. Samples submitted for bio-assay were analyzed for uranium content and concentration using fluorimetric methods of analysis. Techniques used and problems encountered are discussed.

Urinary uranium concentrations range from 38 mg/l, four hours after the incident occurred, to 0.02 mg/l some ninety days after the incident.

A complete review of the urinary uranium data and uranium content of other biological samples, such as blood, skin tissue, blister fluid, feces, etc., are presented.

Data and interpretations are discussed.
Cs$^{137}$ EXCRETION AND RETENTION FOLLOWING SINGLE EXPOSURE*

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San Diego, California

N. S. MacDonald
University of California Medical Center
Department of Biophysics and Nuclear Medicine
900 Veterans Ave.
Los Angeles, California

Periodic whole-body counting and excretion analyses were performed on a subject incurring a 5-10 μc internal dose of Cs-137. Data are presented correlating urine and fecal excretion with whole-body counts. A single exponential retention equation was obtained during the period of study, 186 to 579 days post-exposure. Retention half-time during this period was about 80 days.

* Published in:
Health Physics, Vol. 9, 523-528 (May 1963).
Since the beginning of the atomic energy program, the detection and determination of internal contamination by radioactive nuclides has depended primarily on radiochemical examination of urine. Many of the procedures are relatively sophisticated, employing extensive chemical separations on samples as large as several liters. The rapidly accumulating evidence from the in vivo determination of activity in the human body by whole-body counting now shows very clearly that urinalysis is not the reliable monitoring technique for detection of internal contamination that has heretofore been imagined. During nearly two years of full-scale whole-body counting at the NRTS, many radionuclides have been identified in the body that could not be detected in the urine even in a 24-hour sample. Although none of the exposures was high enough to have any biological significance, exclusive of the SL-1 incident, levels have been found as high as 1 or 2 uc and were easily detectable by the whole-body counting techniques employed. For example, in six different incidences each involving primarily only one of the isotopes Sb-125, Ag-110, Co-60, Zn-65, Zr-95 and Cr-51, excellent whole-body spectra were obtained from quantities larger than about 0.01 uc. Concurrent analyses of fecal and urine excretia showed the main elimination route to be by way of the feces with so little voided in the urine as to be undetectable even on a 24-hour sample. Although antimony, silver and zirconium might be expected in the feces because of the possibility of insoluble forms, chromium, cobalt and particularly zinc are easily soluble in body fluids and might be expected in the urine, at least in part. The conclusion seems inescapable that the metabolic fate and mode of excretion of inhaled radionuclides will be more dependent on the physical properties
of the particle with which the radionuclide is associated than with the ionic, periodic-table chemistry of the element. Fecal analysis would be much more inclusive as a detection device than urinalysis but involves even more formidable problems of collection, storage, transport and interpretation for general use. However, such samples provide invaluable information and are used in special cases at the NRTS employing both chemical separation and direct counting in a large gamma well counter. Iodine is the main isotope for which urinalysis is not only adequate but indicated. Urinalysis is also useful in determination of internal dose from those isotopes which, having been deposited in body organs other than the lungs, will be voided in the urine.

The answer to the problem of detection of internal contamination most certainly lies in the very elegant techniques of whole-body counting. It is rapid and convenient and gives both qualitative identification and quantitative determination of all the gamma-emitting isotopes in the body. Furthermore, cost is no longer a limiting consideration that restricts whole-body counting to the larger and more generously endowed laboratories. One does not need the highly sophisticated counters involving expensive shields and 400-channel analyzers to obtain very valuable and adequate information for practical protection. Preliminary experiments in our laboratory show that about 0.1 μc. of many of the gamma-emitting nuclides can be determined without shielding the subject more than that provided in the concrete walls of the laboratory. An inexpensive 2-inch lead shield is used around the crystal detector itself.
PLUTONIUM ANALYSIS OF TISSUES

M. F. Milligan, Jean McClelland, and W. D. Moss
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

The results of experimental work utilizing parenteral administration of plutonium have suggested that the skeleton and the liver may be critical organs in plutonium exposure. Later data obtained by the analysis of fortuitous autopsy samples indicate that, at least for inhalation exposures, the lymph node may in fact be the critical organ.

The present study, undertaken to elucidate the factors governing storage in the body, is described in detail.
RADIOLOGICAL CHEMISTRY ASSOCIATED WITH THE HANFORD CRITICALITY OF APRIL 7, 1962

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General Electric Company
Hanford Atomic Products Operation
Richland, Washington

A critical accident occurred at the Hanford Atomic Products Operation at 10:59 a.m. on Saturday, April 7, 1962. Three men received radiation doses exceeding one rad and were hospitalized while medical observations and estimates of their radiation doses were made. The radiochemical and bio-assay measurements in connection with the accident are reported. Blood Na\textsubscript{24} measurements and whole body counting provided the primary and early information on the neutron exposure. Measurements of the P\textsubscript{32} in hair produced by the S\textsubscript{32} (n,p) P\textsubscript{32} reaction provided information for estimating the fast neutron dose at various locations on the individuals.

Additional information on the neutron exposure was obtained from measurements of the induced radionuclides in the silver absorbers from the personal dosimeters and from the employees' personal effects. The time-integrated neutron flux to which these objects were exposed was determined by re-exposing these objects to a known slow neutron flux in the moderator of a Van de Graaff accelerator and re-measuring the induced radionuclides.

The Na\textsubscript{24} elimination in urine and feces samples was determined from measurements made for several days after the incident.
The release of the short lived fission product Cs$^{138}$ (32.2 min.) from the building ventilation exhaust system served as a monitor of the relative rate of the continuing fission process in the criticality vessel.
Investigations of the toxicology and mineralogy of thorium requires its determination at extremely low concentrations in many kinds of biological and mineralogical materials. An efficient method is required for separation of thorium from the relatively large samples employed. In previous work, thorium was observed to accompany barium sulfate to a surprising extent considering the solubility of thorium sulfate. The present investigation has shown that thorium will precipitate on any insoluble sulfate and that the process is an extremely efficient and reliable one. Precipitation of 25 mg. of barium as sulfate will separate greater than 99.5% of the thorium from 100 µg. down to at least 10⁻⁵ µg. in 75-ml. volume. Since the fluorometric procedure developed in this laboratory will not measure more than 5 µg., the range is highly satisfactory. The separation takes place from strongly acidic solutions containing high concentrations of alkali metal sulfates and is not affected by concentration or type of acid, temperature of precipitation or length of digestion, or presence of high concentrations of most other elements including phosphates. Pyrosulfate fusion is employed for dissolution of various kinds of refractory materials including thorium itself. The aqueous filtrate from the barium sulfate precipitation contains most of the other components of the sample and is discarded. The barium sulfate is dissolved in alkaline DTPA and the thorium determined directly in the alkaline solution by the fluorometric procedure previously described. The effect of
experimental conditions and most of the elements of the periodic table have been checked exhaustively using $2 \times 10^5$ cpm of thorium $^{234}$ as tracer. The procedure has been applied to the following types of samples with the detection limits indicated: rocks, $2 \times 10^{-6}$%; bone ash, $5 \times 10^{-7}$%; feces, liver, and grain, $2 \times 10^{-8}$%; urine, $10^{-11}$ g/ml; and blood, $2 \times 10^{-10}$ g/ml.