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Proceedings of the
10th Annual
**BIO-ASSAY and
ANALYTICAL
CHEMISTRY
MEETING**

held at
Cincinnati, Ohio

October 8-9, 1964

United States

Atomic Energy Commission
Division of Technical Information

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PROCEEDINGS OF THE TENTH ANNUAL MEETING ON
BIO-ASSAY AND ANALYTICAL CHEMISTRY

October 8-9, 1964
Cincinnati, Ohio

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INTRODUCTION

The Tenth Annual Meeting on Bio-Assay and Analytical Chemistry was held at the Netherland-Hilton Hotel, Cincinnati, Ohio, on October 8 and 9, 1964. This meeting, as well as the first annual meeting held in 1955, was sponsored by the National Lead Company of Ohio, operators of the AEC feed materials production center at Fernald, Ohio.

Proceedings of previous meetings were issued as AEC reports NLCO-595 (1955), WASH-736 (1956), WASH-1023 (1958), TID-7591 (1959), TID-7616 (1960), ANL-6637 (1961), DP-831 (1962), and TID-7696 (1963). Proceedings of the 1957 meeting were not published.

Purpose of these meetings is to provide an opportunity for AEC and AEC Contractor personnel to discuss procedures and problems associated with the collection, interpretation, and application of health protection data.

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REPORT OF BIO-ASSAY ACTIVITIES AT SAVANNAH RIVER PLANT

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BIO-ASSAY AND THE LAW

W. J. Grannen, G. C. Smith, and J. A. Quigley, M.D.,

ADDRESS OF WELCOME

G. W. Wunder, Manager
Nuclear Metals Division
National Lead Company

I am glad for this opportunity to welcome all of you to Cincinnati for your tenth annual meeting. This is a much larger group than the one I welcomed at the opening of your first meeting at Fernald in 1955. As I recall, there were about 25 or 30 people at that first session. It pleases me to see that you have found these meetings worthwhile enough to make them an annual affair. Judging from the size of the group here today, your enthusiasm has not dwindled.

At the time of your first meeting the field of atomic energy was relatively new to us, and we were having our share of problems. One operation which gave us particular trouble at Fernald was our thorium plant. Here, mantle grade thorium nitrate was converted through various intermediate steps into thorium metal fuel elements for reactors. By 1955 we had our thorium production problems pretty well licked, but we were experiencing high concentrations of alpha emitting material in the air.

Our health and safety people were looking for methods which would give them a better evaluation of this thorium problem and recognized a need for better bio-assay procedures. Bill Hoover, head of our Bio-Assay Lab at the time, came to the conclusion that it would be helpful if people actively engaged in the field of bio-assay and analytical chemistry could get together for an informal discussion of mutual problems and an exchange of ideas. As a result of this suggestion, your first meeting was held.

We at National Lead feel that we gained a great deal from that first meeting and that we have continued to profit from succeeding meetings.

We have adapted to our needs some of the procedures for uranium, thorium, and radium analyses which have been presented at these meetings. We have been able to improve our procedures for these and other materials with which we must be concerned. Information which has come from this group has been useful to both AEC contractors and private industry who work with materials on which you have reported.

Probably one of the greatest benefits of these meetings is the opportunity they provide to exchange information and ideas regarding the development and application of protection guides. Some of you have worked on committees which develop these standards. If there is some doubt about our interpretations of standards or their application, it is reassuring to get the word from people who are in the know about these matters. Some of you have assisted us with our bio-assay problems; we hope that we have been of some assistance to you.

Though we have gained much in the past ten years, we hope to accomplish even more in the future. As most of you know, we have a particular interest in the collection of data on human exposure to uranium and the resultant concentrations of uranium found in various organs of the body. We have had a faint hope that the information that we have gathered would be useful in arriving at a maximum permissible concentration for uranium in air which could be met at less cost. Progress in obtaining this information is slow. We would like to encourage others who have the opportunity to get tissue from autopsies to help in this project.

We have from the beginning been concerned with the legal aspects of our exposure evaluation and protection program. I see from the program that there will be some discussion of this in your last session. This is a

matter of great importance to the AEC and its contractors, but it is of even greater concern to private industry. The AEC and its contractors can afford publicity about health problems more than private industry can. Publicity for the private enterpriser can put him out of business.

All of us in the atomic energy program have been affected by the cost reduction efforts of the Commission. Reduced cost, which will make atomic energy economically competitive with other forms of energy, is good for all of us. I subscribe to cost reduction, but it is never our intent to sacrifice safety when reducing costs. As I see it, you people in bio-assay and analytical work may have to move in two directions. On the one hand, with much talk about the threshold theory, more information will be needed regarding the relationship between exposure at low levels and biological effects. This may require improvements in analytical methods to provide reliable measurement at very low concentrations. You will have to develop new analytical techniques and new instruments; this is usually costly. On the other hand, you should be trying to develop less expensive but adequate methods to give results sufficiently reliable for day-to-day control.

I am happy to welcome you to Cincinnati, and I am glad that you accepted our invitation to come here this year for your meeting. I wish you a very successful two days.

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RECENT BIO-ASSAY ACTIVITIES AT
NATIONAL LEAD COMPANY OF OHIO

Michael W. Boback
Richard C. Heatherton

National Lead Company of Ohio
Cincinnati, Ohio

This report summarizes some recent non-routine problems which have occupied the interest of the Bio-Assay Department, Health & Safety Division, National Lead Company of Ohio. Several of them are still under consideration and may be discussed in future reports of this type. In most cases, the work described here was done in cooperation with the Industrial Hygiene & Radiation Department and other departments in the Health & Safety Division.

FUSION OF NaF, FLUOROMETRIC DETERMINATION OF URANIUM

In the fluorometric determination of uranium, 0.1 milliliter of sample is pipetted into each of three platinum dishes. After evaporation on a hot plate the sample residue is fused with 200 milligrams of sodium fluoride. A single gas burner is used for the fusion which requires 30 to 40 seconds at a temperature of about 1000°C. Our monthly sample load requires about 4000 separate fusions which include the fusion of blanks, controls, standards, and samples.

Induction heating and infrared radiation were considered as two possible heat sources which could increase the speed and accuracy of the uranium determination. We tried both of these systems without success. We did, however, establish some of the conditions required for a successful system. A portable infrared unit was obtained from the Fostoria Corporation, Fostoria, Ohio. The unit consisted of four quartz lamps which operated at a power density of 200 watts per inch. Each lamp was 11-3/4 inches long, 3/8 inches in diameter, and contained a 10-inch tungsten filament. The lamps, 1/2 inch apart, were housed in a machined quartz-rock refractory, which was enclosed on five sides by a metal frame. Approximate over-all size of the unit was 4 inches by 8 inches by 16 inches. The first tests were made with the unit supported over one or more platinum dishes which were placed on a layer of fire-brick. Complete melting of the NaF required about 30 seconds. Simultaneous fusion of two or more dishes could not be attained - the heat gradient was too great. Fumes from the NaF soon began to etch the quartz lamps, so further tests were made with the dishes suspended over the lamps. See Figure I. Platinum crucible covers and large platinum vessels were placed over the dishes as reflectors. Reproducible simultaneous fusion could not be obtained in this manner. Further tests were made in the Fostoria Corp. laboratory with a larger furnace. For the tests, six dishes were suspended over the lamps and then a gold-plated, water-cooled reflector plate was placed above the samples. Reproducible simultaneous fusion could not be obtained, despite the fact that the six dishes occupied only a fraction of the total furnace area.

The fusion tests with induction heating were made with a coil made available by Lepel High Frequency Laboratory, New York, New York. The first tests were carried out in air and the fused pellets were deeply stained. A Plexiglass box was built to house the coil so that a nitrogen atmosphere could be maintained. See Figure II. This arrangement prevented stains. However, simultaneous fusions of two or more dishes were not attained. The problem, as before, was that of variation in heating.

These tests indicated that a suitable system might be possible with a turntable that would move all samples over the same path during the fusion period. In a infrared system, the turntable would have to be within the furnace. In a induction heating system, the turntable would provide all dishes with the same path within the influence of the coil. In addition, it would be necessary to provide an inert atmosphere to prevent the staining of the fused pellet. These ideas were not pursued. Estimated costs and design uncertainties place these systems in a research category outside of our consideration. An infrared furnace similar to the one used at the Fostoria Laboratory would cost about \$2300. This price does not include a turntable or arrangements for an inert atmosphere. An induction heating unit to produce 10 fusions per minute would cost about \$6000 and a unit to produce 50 fusions per minute would cost about \$7600. These two prices include a turntable but do not include arrangements for an inert atmosphere.

URANIUM IN LUNG AND LYMPH NODE TISSUES

Lung and lymph node tissues from six hospital autopsy cases were analyzed for uranium. These persons had not been company employees and had no known exposures to uranium. The concentrations of uranium found in the lung tissues were similar to levels found in other unexposed persons and employees at this site who had low or moderate exposures.⁽¹⁾ No uranium was found in the lymph nodes.

The primary reason for these analyses was to determine if the lymph nodes of unexposed persons concentrate the low amount of uranium which an unexposed person would breathe. The concentration of uranium by lymph nodes has been well established by the exposure of animals to high levels of uranium. Concentration by the lymph nodes has also been predicted for the lower exposures which would be encountered in a uranium industry. The predicted levels have not been found in the few cases where lung and lymph node tissues from National Lead Company of Ohio personnel have been analyzed.

The only lymph nodes obtained were the perihilar nodes which were buried in the lung tissue. The more abundant mediastinal nodes, which are located along the trachea, were not included in the tissue. We estimate that we obtained less than 25% of the lung nodes.

PASSIVITY OF URANIUM SLIVERS IN HAND INJURIES

During a clean-up campaign, two workers received minor hand injuries from slivers of scrap natural uranium. In

one man's case, the sliver remained in his hand for four days. Daily pre-shift urine samples from both men did not indicate any noticeable absorption of uranium due to the metal fragments.

One sliver was recovered and analyzed for uranium. It weighed 50 milligrams and was 86% uranium. This scrap was generated in 1958, and oxidation is the probable cause of the low uranium content.

RADIUM FROM REMELT OPERATIONS

Considerable amounts of radium-226 were found in alcohol solutions used to wash components of our Alphatron vacuum indicators. These Alphatron instruments are used on furnaces in which uranium is remelted under vacuum. Alpha particles are emitted by a 0.1-0.2 millicurie radium source. These particles travel to a sensing head. The number of particles reaching the sensing head is proportional to the vacuum in the furnace chamber. With continued use, the components which open into the vacuum become coated with residues from the remelt crucible. An ethyl alcohol wash is used to remove the residues.

We have found 5200 μg Ra-226 in a liter of solution which was used to wash out only six different instruments. And we have found as little as 18 μg after four instruments were washed. Radium separated from these solutions followed the build-up of pure Ra-226.

According to the manufacturer, the radium is plated on a metal source and covered with a thin plating which helps

to protect the radium. The plating is thin enough to allow the alpha particles to pass. A small amount of radon is lost from the source.

We decided that as long as the instruments and wash solutions were handled with caution, there was no hazard associated with the cleaning of these instruments. There is no hazard in the release of this radium into the plant effluent. The normal plant effluent would give a dilution factor of almost 10^7 and dilution at the river would add a factor of 10^2 .

Some consideration was given to the possibility of the radium arising from the residue produced in remelting uranium. Impurities in the metal, such as uranium daughter products, move to the surface of the metal and may be volatilized. Some of this volatilized material collects on the crucible lid. Radium should have been present on the crucible lid if the radium in the Alphatrons came from the remelted metal. Two samples of residue were analyzed for radium. One sample was collected from furnaces used to remelt enriched uranium and one sample was taken from furnaces used for normal uranium. See Table I. Results in the table are given in disintegrations per minute per gram (d/m/g).

TABLE I Radium in Residue from Crucible Lids

<u>Location</u>	<u>Ra-226</u>	<u>Ra-224</u>
Normal U Furnaces	0.12 d/m/g	30 d/m/g
Enriched U Furnaces	0.28 d/m/g	100 d/m/g

The radium-226 levels were not surprising but the high levels of radium-224 were unexpected. Our interest in these radium isotopes will continue until we have determined the source of the Ra-224 and its distribution.

PLANT RADIATION LEVELS

From 1960 to 1963, we experienced an increase in the external gamma exposures as determined by film badge measurements. The increase does not present a serious problem since all exposures have been below permissible levels. However, a trend is evident and the Industrial Hygiene & Radiation Department, which is responsible for control of radiation exposures, has given consideration to several possible causes. We do not believe that any changes in our film badge program could have accounted for the steady increase.

One probable cause of increased radiation levels is the increased age of the material with which we are working. Uranium which has been freshly separated from its daughter products has a low level of gamma activity. The first two daughters, Th-234, and Pa-234, build in with a half-life of 24.1 days, increasing the gamma activity. At about three months after separation, the uranium daughters reach 93% of their equilibrium activity.

Increased uranium age is the result of changes in production requirements and plant procedures. Some of the more important of these changes are listed below.

- (1) Several years ago we added the production of uranium with a U-235 enrichment of approximately 1%. The current handling of different low enrichments plus normal uranium requires that the work be done in campaigns to minimize isotopic crossover and to insure nuclear safety control. Campaigns mean greater hold-time which allows the build-up of of uranium daughters.
- (2) Our refinery, which produced UO_3 , closed in 1962 and since then UO_3 has come from off-site. This off-site UO_3 starts through the plant older than did the UO_3 which we produced.
- (3) Some of our ingots are now shipped off-site for extrusion and then returned to us for final machining. The added extrusion step means that the metal will be older and therefore more radioactive when it is finally machined.
- (4) Metal from a direct reduction process is now shipped to us with an accumulation of surface impurities, including beta and gamma-emitting uranium daughters. Previously, the metal surface was mechanically cleaned before the metal was shipped.
- (5) Some of the off-site UO_3 is produced from uranium which is recovered from irradiated fuel elements.

Gamma activity in this recycled UO_3 is higher than activity in off-site UO_3 produced from natural uranium because of both greater age and the presence of fission products.

We have tried to determine if there is any variation in the surface dose from uranium metal caused by isotopic variations or process variations. Dosimetry film was placed against the surface of several extruded cores and ingot slices. This was repeated at various intervals until the metals reached radioactive equilibrium. The observed surface doses were higher than the calculated surface doses when the metals were 20 to 40 days old. At equilibrium, all beta surface doses were equal. No conclusions could be made concerning the gamma doses because of the metal thickness. Maximum range of the gamma of interest (from Pa-234) is about 2-1/8 inches in uranium metal. Some of the pieces which we used were only 1/2 inch thick. Gamma radiation from these metals was only a fraction of the surface gamma from metals which are over 2-1/8 inches thick.

This subject of increased radiation levels will be given further study. We hope to learn more about the activity levels in off-site UO_3 , presence of nuclides which contribute to the radiation in recycled UO_3 , and the levels of gamma radiation from uranium metal from different sources.

URANIUM IN FECAL SAMPLES

Two years ago, at the meeting held at Savannah River, the subject of fecal samples was discussed.⁽²⁾ It appeared that we should know more about levels of uranium in the feces of industrially exposed persons. As a result, we have collected fecal samples on three separate occasions in an attempt to increase our knowledge of the fate of inhaled uranium.

Four men were involved in the first study. Fecal and urine samples were collected before and after several off-work periods, including weekends and a two-week vacation period. The calculated daily intake of uranium for the four men ranged from 640 to 1200 d/m. Daily elimination via the feces was from 60 to 10,000 d/m. The relationship between these intake levels and fecal uranium is a tenuous one. Fecal uranium did increase with consecutive days worked. However, this relationship may be due to a chance combination of varying individual samples. See Table II. In Table II, results are given for individual samples collected after periods of 1 to 6 consecutive days worked. In several cases, more than one result is listed for an employee for a given period. The samples were collected over an interval of several months which made it possible to obtain repeated samples in any particular period.

Two men were involved in a second study on fecal samples which was made to help explain why we found relatively high levels of airborne uranium at their particular operation,

but low levels of uranium in their urine. Both men worked together in blending residues to obtain a suitable material for uranium recovery.

TABLE II Uranium in Fecal Samples

Consecutive Days Worked	<u>Employee A</u>	<u>Employee B</u>	<u>Employee C</u>	<u>Employee D</u>	Average
	Uranium, d/m/sample				
1	83, 220	-	-	83, 250	162
2	230, 310	-	-	64	202
3	3700	180	2250, 2250	1500	1970
4	630, 675	900	630, 1160 1200, 2850 9500	-	2180
5	-	-	-	2720	-
6	-	-	-	885	-
Average	830	670	2820	1090	-

Two-stage air dust samples were collected during the performance of that job which caused the highest levels of airborne uranium and for which respirators were worn. Routine air dust samples were taken at other times. Each man wore a respirator for a total of 4 hours per 8-hour shift. Filters in the respirators worn by the men were changed and collected twice each day. Pre-shift and post-shift urine samples were collected over an 11-day period. Fecal samples were collected at the beginning, middle, and at the end of the work week.

Average air dust concentration obtained from the two-stage samples was 3200 d/m/m³. Only 3% to 6% of this total was found in the respirable fraction. We found that the respirator filters collected about 4500 d/m during the four hours of use each day. Average daily elimination via the

feces was 270 d/m and elimination via the urine was 90 d/m. As in the first study, the fecal uranium increased during the work week. Using the data from the two-stage samples, the routine air dust data, an average work schedule, and an assumed respirator efficiency of 90%, we calculated a daily intake of 340 d/m. The average fecal and urinary uranium daily output was 360 d/m. We can only conclude that the respirators were doing the job for which they were intended.

Fecal samples were collected on one other occasion because of possible accidental exposure to UF_6 . During the transfer of UF_6 from one container to another, a distorted gasket allowed the escape of about 900 grams of material. The operation was being carried out in a fume hood and one employee was standing near the release point. Urine and fecal samples were collected for several days following the incident. Only background amounts of uranium were found.

Data from the investigations are meager for drawing definite conclusions. However, the information collected so far leads us to believe that most of the uranium taken in by inhalation or ingestion will be eliminated rapidly in the feces and urine. With higher exposures, the fecal uranium will increase faster than the urinary uranium, probably because of particle size and solubility relationships.

We intend to maintain fecal sampling as an adjunct to the urine sampling program. In cases of possible acute exposure, fecal samples should prove helpful in establishing if an exposure has definitely occurred.

RADIONUCLIDES IN WASTE STREAM

Efforts were made to identify the major radionuclides in a storm sewer effluent which occurs during periods of heavy precipitation run-off. The outfall leads to a stream which leaves the plant site and flows through several miles of farm land before joining the Miami River. Dilution in the small stream is only about 1:1 and, occasionally, our contribution may exceed the natural flow.

Most of the alpha activity was due to uranium and the beta activity due to Th-234 and Pa-234. These radionuclides were well below the maximum permissible concentrations. Radium-224, Ra-226, and Ra-228 were the only other nuclides present at significant levels. The concentrations of Ra-226, a daughter of U-238, and Ra-228, a daughter of Th-232, exceeded the maximum permissible concentration in several samples. However, we do not consider the stream a problem in view of the considerations discussed in Handbook 69.(3) This particular storm sewer waste and the receiving stream have an intermittent flow, present only 15% of the time. We found that when there is flow, Ra-226 and Ra-228 are usually at less than the maximum permissible concentration level. When they are exceeded, the maximum permissible concentration values are not exceeded by more than 30%. The stream which receives this waste is not a clean stream. Just below our plant, a three-inch pipe adds the effluent from a private sewage disposal system. It is doubtful that this small stream is used for humans or for stock water during its flow from the plant fence to the Miami River. The dilution at the Miami River, usually

greater than 100:1, reduces all radionuclides to a concentration well below maximum permissible concentration values. We feel that this is a reasonable manner in which to consider this particular waste and the receiving stream.

When the Ra-224 and Ra-226 appeared in the storm sewer water, there was no work being done with thorium or with radium-containing uranium ore. The last major work with these materials occurred in 1955. Some thorium-containing materials are still stored in two areas. They have been handled occasionally, when wastes were removed for final disposal or when recoverable thorium was shipped to a site engaged in thorium processing. The appearance of these nuclides at this time indicates that material handled in large quantities will require some consideration long after that material is removed from the production processes.

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FIGURE I Portable Infrared Furnace

FIGURE II Induction Coil

X

REPORT OF BIOASSAY ACTIVITIES AT ARGONNE NATIONAL LABORATORY

William D. Fairman
Argonne National Laboratory*

ABSTRACT

A review of recently completed and in progress analytical and instrumental techniques is presented. The review includes work performed by Richard Fredricks, Jean Robinson, and Jacob Sedlet, in addition to the author.

Among the items discussed are the following:

1. The determination of iodine-131 in milk and urine by initial exchange of the inorganic iodide onto silver chloride followed by solvent extraction and coprecipitation with silver iodide. (Halide-silver halide exchange reactions, foam extraction and direct-plating and exposure effects are also discussed.)
2. The determination of promethium-147 in urine by extraction into 2-diethylhexyl phosphoric acid-benzene, followed by liquid scintillation counting of the organic extract.
3. Sequential determination of uranium, neptunium, and plutonium in urine by use of triisooctylamine-xylene extractions, anion exchange and electrodeposition.
4. Determination of uranium in urine by extraction into 2-diethylhexyl phosphoric acid-benzene prior to anion exchange and electrodeposition.
5. Determination of technetium(IV)-99 in urine by coprecipitation with ferric hydroxide and oxidation to technetium(VII) with nitric acid, followed by use of the procedure for technetium(VII) reported at the 1963 meeting.
6. A least squares fortran program for the determination of components of radioactive decay mixtures by computer analysis of count-rate data.
7. Applications of multiparameter analysis to bioassay.
- and 8. The determination of astatine-210 and -211 in urine by alpha and gamma spectroscopy and chemical separation by spontaneous deposition on copper or coprecipitation with tellurium.

* Operated by the University of Chicago for the U. S. Atomic Energy Commission.

A PROGRESS REPORT ON RADIOLOGICAL CHEMISTRY AT HANFORD

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Hanford Laboratories
General Electric Company*
Richland, Washington

A major portion of the work recently in progress in the Radiological Chemistry Unit of Hanford Laboratories is included in two of the papers which will be presented later in the meeting. These papers are "The Direct Measurement of Radionuclides in Bio-Assay Samples by Multidimensional Gamma-Ray Spectrometry", by R. W. Perkins, and "Application of Tertiary Amine Extraction to the Determination of Uranium in Biological Materials" by T. M. Beasley. Progress has been made in two additional areas which will be reported here. These areas are Large Area Alpha Spectrometry and Cs¹³⁷ in Human Hair.

Large Area Alpha Spectrometry

Sensitive techniques for measurement of Alpha emitters are now available which can be used to study natural levels in human beings at natural levels of intake and excretion. These techniques were developed mainly by W. V. Manyeord, C. R. Hill, and R. V. Osborne at the Royal Cancer Hospital in England, and are reported in numerous publications. Of special interest to our work at Hanford was the large area alpha spectrometer. In this instrument an alpha emitting radionuclide level of 0.1 pc/g will more than double

*General Electric Company, Richland, Washington. Work performed under Contract No. AT(45-1)-1350 for the U.S. Atomic Energy Commission.

the background and so may be identified and measured by its characteristic alpha energy spectrum. We have constructed at Hanford two large area alpha spectrometers following closely the pattern of those developed by the workers mentioned above. Details of the chambers are shown in the first five slides. The larger chamber is a gridless concentric cylindrical ionization chamber in which the 15000 cm² aluminum coated plastic sheet contains the source and forms the outer electrode. Alpha spectral line widths of the order of 150 kev are normal if the sample has been ground to micron dimensions and sprayed on the sheet at a concentration of 1.5 g per 15000 cm² or less. The smaller chamber is similar to the larger chamber but has an effective source area of about 1200 cm². This chamber has a grid and is capable of somewhat better resolution than the larger chamber. Backgrounds equivalent to a contamination of less than 0.05 dpm per nuclide are obtained with this instrument. Thus levels of about 0.5 pc/g may be determined. The last slide shows a spectrum obtained with the smaller chamber. Sample counting is just now beginning with the large chamber.

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Cs¹³⁷ in Human Hair

The analysis of hair has received interest as a possible means of estimating radioisotope concentrations in the body.^(1,2) Recently in this laboratory we have measured Cs¹³⁷ in the hair of Alaskan Eskimos whose Cs¹³⁷ body burdens are being determined by whole body counting techniques⁽³⁾ in a separate study.

Hair samples ranging in weight from 1-15 g were obtained from both adult male and female Eskimos at Anaktuvuk Pass, Alaska, whose Cs¹³⁷ body burdens from 1963 to 1964 ranged from 0.3 to 1.0 μ /c. The hair samples were washed with large quantities of water, 0.1 M HCl, water, and finally acetone. After drying and weighing, the hair samples were counted, depending on sample size, in either a 5-in. diameter by 5-in. thick NaI(Tl) well crystal surrounded by a large anti-coincidence guard⁽⁴⁾ or a 9-3/8 in. diameter by 8-1/2 in. high NaI(Tl) crystal with a 3-in. diameter well of sufficient depth to accommodate a 500 milliliter polyethylene bottle⁽⁵⁾. Signals from the NaI(Tl) crystals were fed to 400 channel pulse height analyzers. The samples were counted for 500 minutes, with a detection limit (99% confidence level) of 1 picocurie of Cs¹³⁷ for the first system described and 4 picocuries for the larger crystal system.

Each of 20 hair samples measured showed detectable amounts of Cs¹³⁷. When compared to the Cs¹³⁷ body burdens, male hair samples gave concentrations ranging from 3-8 dpm/g of hair/ μ c Cs¹³⁷ in the body while values for the female hair samples showed less consistency and ranges of 1-20 dpm/g of hair/ μ c Cs¹³⁷ in the body.

In addition to the variability expected from person to person the range of values per unit activity of Cs^{137} in the body would be expected to vary since (1) the hair samples did not in each case correspond to the time the whole body count was made, and (2) the samples contained hair which was not all the same age since their formation. More carefully controlled experiments are being conducted to determine the relationships between hair content, intake and body burdens of Cs^{137} in the Alaskan Eskimo. It is interesting to note that the concentration of Cs^{137} in hair on a per gram basis is almost the same as the concentration in urine on a per gram basis.

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POLONIUM URINALYSIS PROCEDURE

By

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ABSTRACT

The urinalysis procedure for the determination of polonium, which had been used for 16 years, was revised. Although the efficiency of each procedure was the same, the count level of the modified procedure was four times greater.

INTRODUCTION

For the past 16 years, the urinalysis procedure for polonium used at Mound Laboratory was based on the early work of R. A. Bell and associates as reported by E. S. Spoerl.¹ The analytical procedure was reported by H. E. Meyer² at the Second Bio-Assay and Analytical Chemistry Meeting. In this procedure (Fig. 1) 50 ml of urine was measured into a paper cup and acidified with 10 ml of 6N HCl. The polonium was deposited on a one-inch diameter copper disk suspended by means of a glass hook in the urine which was stirred for two hours at room temperature. This procedure was used for many years for routine analysis; however, it did not have the required sensitivity to meet the more stringent maximum permissible body burden of 0.04 microcuries.

Two changes were made in the procedure to increase the sensitivity: (1) doubling the volume of the sample being analyzed; and (2) plating one surface of the disk instead of on both sides. These two changes increased the polonium concentration four-fold for each counting determination, simplified the counting operations, and provided a better statistical result without increasing the counting time.

*Mound Laboratory is operated by Monsanto Research Corporation for the U. S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

To accomplish these goals, a plating cell method was adopted. A procedure has been reported where baby bottles were used for plating cells,³ but these bottles were not large enough for our purpose. Preliminary investigations indicated that polonium will deposit spontaneously on stainless steel* equally as well as on copper. This led to the design of a Lucite plating cell, which accommodates a 1-7/8 inch diameter stainless steel disk.

EQUIPMENT

The Lucite plating cell, shown in Figure 2, consists of two parts, a cap and barrel, with an "O" ring seal. The overall dimensions of the cell are 3-1/2 inches in diameter by 4-7/8 inches in height. Five volume marks are circumscribed on the side of the barrel to measure the sample volume in the cell. The heavier line (Fig. 2) is the 100 ml volume mark. A one lobe stirring rod used in the old procedure was replaced with a butterfly stirring rod. Recoveries with the old style stirring rod were 10 to 15% lower with this cell. A Misco Acid dispenser is used to measure and to deliver HCl to each sample. The stirring apparatus used in the old procedure was not changed. (Fig. 1-3) The plated disks are counted in a low background proportional alpha counter (Nuclear Measurements Corp., Model PC-3B).

EXPERIMENTAL

Five Lucite plating cells were fabricated and a series of spiked urine samples were processed to determine the effect of such variables as acid concentration, plating time and stirring speed. Individual urine samples from unexposed individuals were used in these experiments. Spike levels of 8.0 disintegration per minute (d/m), 20 d/m and 80.0 d/m were used. In all experiments, unless otherwise noted, a plating time of two hours and a stirring speed of 450 rpm was used. The Po was plated at room temperature from samples acidified with HCl.

To determine the problem of contamination of the cells, tap water blanks were processed between each set of spikes. No special cleaning effort was made between the spike and blank runs. A total of 230 spikes and blanks were run during the

*Stainless Steel Disk, Metal Type 302, Finish 3B, Stock 0.024-inch

series of experiments. The results of these studies are shown in Tables 1, 2 and 3.

CONCLUSIONS

The change from the old to the new procedure was quite smooth. The amount of labor required for the two methods is about the same. The additional time for set-up and clean-up of the cells is more than offset by the time saved in counting. The recovery of polonium for the two methods is comparable, but the count level of the modified procedure is four times greater than in the old procedure for any given level of exposure. Higher recoveries could be obtained by using an elevated temperature during plating. However, when processing large numbers of samples, this improvement hardly merits the additional apparatus and labor to achieve.

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Table 1

Po RECOVERY AS A FUNCTION OF ACID CONCENTRATION

<u>Acid Conc. (N)</u>	<u>Recovery (%)^a</u>
2.50	92
2.25	67
2.00	85
1.80	75
1.50	82
1.25	82
1.00	84
0.78	80
0.55	80
0.28	91
Average	81.8%

^a Each value is an average of 5 determinations; the spike level was 8.00 d/m.

Table 2

POLONIUM RECOVERY AS A FUNCTION OF PLATING TIME AND STIRRING SPEED^a

<u>Plating Time(hours)</u>	<u>Stirring Speed(rpm)</u>	<u>No. of Samples</u>	<u>Spike Level(d/m)</u>	<u>Recovery (%)</u>
2.0	450	5	20.0	79.2
2.0	600	5	20.0	74.4
1.5	450	3	40.0	80.6
1.5	600	3	40.0	74.0
1.0	450	3	40.0	65.0
1.0	600	3	40.0	69.0
0.5	450	3	40.0	42.3
0.5	600	3	40.0	48.0

^a See Figure 4

Table 3

CONTAMINATION OF TAP WATER BLANKS FOLLOWING 8.0 d/m SPIKED SAMPLES

<u>Range (d/m)</u>	<u>Distribution of Sample</u>	
	<u>(No.)</u>	<u>(%)</u>
0.00 to 0.10	15	30
0.11 to 0.20	10	20
0.21 to 0.30	15	30
0.31 to 0.40	4	8
0.41 to 0.50	2	4
0.51 to 1.0	3	6
> 1.0	1	2

Figure 1 Equipment Used in the "Old" Polonium Urinalysis Procedure

Figure 2 Lucite Plating Cell

Figure 3 Equipment Used in New Polonium Urinalysis Procedure

Figure 4 Polonium Recovery as a Function of Plating Time and Stirring Speed

EFFECTIVE HALF-LIFE OF POLONIUM

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ABSTRACT

Data on the elimination of polonium are presented for two cases of exposure, one by puncture with a contaminated wire and one by inhalation of polonium. The effective half-life of polonium in the inhalation case was 33 days, but the biological half-life of the puncture case was 24 days.

INTRODUCTION

During the past year two employees at Mound Laboratory were exposed inadvertently to polonium-210 while processing this radioisotope.

The number of individual cases reported on the elimination of polonium from the human body are scanty. Spoerl⁴ reported a biological half-life of 36.6 days, but most studies have been made with animals.⁶ Thus, when two employees were accidentally exposed to polonium-210, one by skin puncture and one by inhalation, it was an opportunity to follow the rate of elimination from the body. Since nearly all exposures of record are by inhalation, the puncture case was unique to our operation.

CASE I - POLONIUM EXPOSURE FROM A PUNCTURE

In this case the employee punctured his finger with a highly contaminated platinum wire. The piece of platinum was excised from the finger approximately three hours after the skin was punctured. A urinalysis of a 24 hour urine sample from the

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first day after the exposure showed a polonium concentration of 1200 d/m. On the second day following exposure the polonium level in the 24 hour sample decreased to 350 d/m and continued to decrease with a biological half-life of 24 days. (Fig. 5)

CASE II - POLONIUM INHALATION EXPOSURE

This employee was exposed from the inhalation of polonium in acid vapors. In this case the blood, urine, and feces were analyzed and the data were compared to results obtained from laboratory animals. The effective half-lives of the polonium-210 in Cases I and II are shown in Figure 5. The 24-day effective half-life for Case I (the puncture wound) is much shorter than in inhalation polonium exposures. The half-life value of 33 days for Case II (the inhalation exposure) conforms more closely to the 36.6-day effective half-life value reported by Spoerl.⁴ As may be expected, the mode of intake and the chemical form have a significant influence on the effective half-life.

Several blood samples as well as the urine samples from Case II were analyzed. The blood and urine data are shown in Figure 6. It is interesting to note that both blood and urine follow a 33-day effective half-life elimination. Based on the total volume of blood⁵ for an adult male weighing 165 pounds (Case II) the total activity in the blood was 145 times the amount of activity eliminated per day in the urine. All data on Case II that are available at this time are presented.

The ratio of polonium in the feces and in urine for Case II was determined. A graph, Figure 7, taken from work of R. M. Fink⁶ and associates, shows the elimination rate of polonium in urine and feces for rats. The fecal to urine ratio at 50 days in the rat according to these data is 6.54. One week's total fecal elimination was collected from Case II and analyzed for polonium. Fecal collection began on the 47th day and ended on the 52nd day after exposure. The results and a comparison to the rat data are shown in Table 4. These data are in remarkable agreement.

Table 4

POLONIUM-210 EXCRETION

RAT DATA COMPARED TO HUMAN DATA

CASE II

TOTAL FECAL AND URINE EXCRETION FOR ONE WEEK

47TH THRU 52ND DAY

Total Feces	50,000 D/M	6.54 Ratio
Total Urine	7,000 D/M	

RAT DATA

85% / Day / Body Content	6.49 Ratio
13% / Day / Body Content

Figure 5 Urinary Elimination of Polonium (d/m for 24 hour urine sample) Cases I and II

Figure 6 Relative Blood and Urine Concentration
of Case II Polonium Exposure

Figure 7 Total Rate of Elimination of Polonium from Body as Percent of Body Content (with the relative contributions of urinary excretion, fecal excretion and radioactive decay)

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URINARY ELIMINATION
FOLLOWING INHALATION OF INSOLUBLE PLUTONIUM OXIDE

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ABSTRACT

From two inhalation exposure cases of plutonium oxide the urinalysis data indicate that DTPA treatments are the most effective from 100 to 300 days after exposure.

INTRODUCTION

Data on the elimination of plutonium from the body are scanty, as is the case for most radioisotopes. As might be expected, the mode of intake has a significant influence on the elimination rate.

The expression for the elimination of soluble plutonium in urine is described by W. H. Langham⁷ as a power function. The line designated 0.04 μ c is the curve for Langham's power function for urinary elimination of plutonium as shown in Figure 8. Another exposure case shown in Figure 9 resulted from the inhalation of plutonium oxide. The data from this case do not follow the power function expression due to the retention of plutonium by the lungs. In Figure 10 the data plotted on semilog paper follow a 700 day exponential elimination, which is the pattern of elimination in urine that we have observed from those individuals with plutonium oxide inhalation exposures. The data presented here deal with the oxide inhalation type of exposure and the use of Calcium Chel 330, brand of calcium trisodium penthalmil, (DTPA)* in these cases. For the benefit of comparison, the data from an inhalation exposure to plutonium nitrate, a soluble compound, are shown in Figure 8.

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CASE I - PLUTONIUM OXIDE INHALATION

Case I shown in Figure 11, is an oxide inhalation exposure in which intravenous treatment of DTPA* were started on the 75th day after exposure. Treatments of one-gram of DTPA per day for five days a week were given for three weeks. Two single treatments were administered three weeks later and were the last given to this employee. The urine level prior to treatment had gradually increased to 5.36 d/m. The first urine sample following the treatment was 210 d/m and a high of 272 d/m was recorded on the fourth day of treatment, a 40 to 50-fold increase.

Two 700-day half-life curves were plotted in Figure 11. The upper curve describes the expected levels in the urine if DTPA had not been administered. The lower curve shows the actual data. A comparison of the intercept of these two curves at 700 days indicates a urine level of approximately one third the expected value based on other oxide exposures. If the body burden is directly related to urine level, it would seem that the series of DTPA treatments in effect reduced the body burden by a factor of three. This, however, is difficult to believe in view of the actual amounts of plutonium removed during and immediately following the treatment period.

CASE II - PLUTONIUM OXIDE INHALATION

Case II shown in Figure 12 was given one gram of DTPA by intravenous injection the day the exposure occurred and continued with one gram treatments each work day for two weeks and two days. During the next month one treatment a week was given. On the 53rd day after exposure a three week daily* series was started and followed with three once a week treatments. After a three months' rest period a third daily series of three weeks' duration was started 212 days after exposure. Peak urine levels of approximately 70 d/m, 90 d/m, and 330 d/m, respectively, were recorded during the first, second and third series of treatments.

CONCLUSIONS

A study of the data from these two oxide exposures demonstrates that the effective use of DTPA depends on the availability of the plutonium. In the oxide inhalation exposure the period

*Excluding Saturday and Sunday

immediately following deposition is apparently the least effective period for treatment due to retention in the lungs. The period of 100 to 300 days following exposure is possibly the optimum period as the urine level on untreated oxide exposure cases reaches its peak during this period. The gradual increase in the urine count during the initial 100 day period also permits a wait-and-see policy concerning the use of DTPA. Also, some estimate of the body burden can be made before the normal elimination is disturbed by the use of DTPA.

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The author wishes to thank H. W. Meyer in the review of these reports.

Figure 8 Urinary Elimination of Plutonium Following Exposure to Plutonium Nitrate, Log-log Plot.

Figure 9 Urinary Elimination of Plutonium Following Exposure to Plutonium-238 Oxide, Log-log Plot.

Figure 10 Urinary Elimination of Plutonium Following Exposure to Plutonium-238 Oxide, Semi-log Plot

Figure 11 Plutonium-238 Oxide Exposure Case I

Figure 12 Plutonium-238 Oxide Exposure Case II

THE PHYSICAL PARAMETERS OF PARTICULATES WHICH EFFECT RESPIRATORY TRACT DEPOSITION

by Robert G. Thomas

It has been approximately five years since Morrow and Casarett from the University of Rochester discussed deposition and retention of particulates in the respiratory tract before this Group.^(1, 2) This presentation will be somewhat different from theirs and will attempt to review certain physical and physiological parameters which effect the pattern of deposition. The first part will be a discussion of the various properties of the respiratory tract and will include an indication how, theoretically, one can determine from certain particle characteristics why deposition occurs where it does. Following these rather straightforward interpretations it will be shown how the practical aspects of estimating respiratory tract deposition is suffering from lack of good data, both from experimentation and industrial exposures. Much of the material to be presented was organized by Dr. T. T. Mercer of the Lovelace Foundation and many of the calculations were carried out by him.

Figure 1 shows a cross-section of the nasal-pharyngeal region and indicates the anatomical regions which relate to the deposition of particles within the upper respiratory tract.⁽³⁾ For instance, one sees the various turbinates which occupy the nasal passages and which are coated with a mucous layer which is capable of removing particles upon contact. These turbinates are likened to a maze through which the air streams are drawn and in which impingement and impaction can occur to enhance removal of particles. It should also be noted that the oral cavity does not have anything approaching this maze of tubes to filter out particulates upon entrance to the body. The importance of this upper respiratory tract, the nose and/or the mouth, will be discussed later.

Figure 2 is a cutaway view of the respiratory tract below the larynx and indicates the various branches of the air passages.⁽⁴⁾ It shows how the relative size of the tubes decreases starting with the first major bifurcation and passing through the main bronchi, upper and lower bronchi and down into the bronchioles in the extremities of the lobes.

Figure 3 shows essentially the same material but here a section of one of the lower respiratory passages has been exploded to indicate the areas where oxygen exchange occurs.⁽⁵⁾ This gives an excellent idea of the tube diameters involved in the lower respiratory tract where they decrease from 0.6 to 0.2 mm in the alveolar

duct. Beyond this, where most oxygen exchange occurs, are the tiny aveoli which make up the alveolar sac. Table 1 lists a more comprehensive quantitative sizing of the respiratory tubes plus a branching factor to estimate the total of each type passageway to be expected. These data are from Findeisen's famous work and show the tremendous number of branches involved, reaching over 50 million where the alveolar sacs are concerned.⁽⁶⁾ The diameters and length of each are also shown to emphasize the dramatic differences in relative sizes. Another diagrammatic version of the respiratory tract from the entrance of the trachea down to the alveolar region is shown in Figure 4.⁽⁷⁾ At the risk of belaboring a point this is included to indicate the type of velocities which occur in the air streams which ventilate the respiratory tract. In the trachea and upper respiratory bronchioles the velocity of the air in cm/sec is around 125 - 200 but as the smaller bronchioles are reached this decreases considerably. The velocity of the air stream in the trachea is approximately 150 times that which is found in the lower bronchioles where they enter the aveolar spaces. This means that the particulates which are carried down to these lower regions are moving at an extremely lower rate and at the alveolus this reaches zero. With these velocities it requires a transit time of 1/4 second for a particle to pass from the mouth to the segmental bronchi but requires an additional 2 1/2 seconds to reach the alveolus.

The preceding Figures have shown in detail the gross anatomy of the respiratory tract and have emphasized the parameters which effect particulate deposition, mostly in terms of size, numbers and velocities. This background makes it easier to describe the four methods by which deposition takes place, namely by impaction, interception, sedimentation and Brownian motion. These are described in Table 2 in which P is the probability of a particle being deposited, m is the mass of the particle and d its diameter, u is the linear velocity, a is diameter of the tube (air passage), t is time and z is a parameter which essentially is an inverse function of resistance. Part of z deals with the distance between or mean free path of the air molecules through which the particle moves. The functions were described in this manner by Mercer and it proves to be a very convenient method of presentation for understanding the basic variables involved. Impaction is fairly straightforward and prevails mainly at bifurcations where the air stream has to bend to enter the next segment of the respiratory tract. As it does so, the particle may have sufficient linear velocity and mass so its tangential force will throw it against the wall where it deposits on the mucous membrane. It is obvious that the parameters shown will play an important part in this particular means of deposition. The probability of hitting the wall is directly

proportional to the mass and velocity of the particle and inversely proportional to the diameter of the air passage. Interception is the second process and it too is straightforward, depending only upon the diameter of the particle and the diameter of the tube. If the particle diameter increases and the diameter of the air passage decreases the probability of contact is greater. Next is sedimentation which depends upon mass, time of residence of the particulate and size of passageway. This rate of fall due to gravity also depends upon the resistance offered by the air through which it travels. The fourth process of importance is that known as Brownian motion or diffusion. This is the complicated process by which extremely small particles have internal energy imparted to them which thereby allows them to move in random transversal directions. The average velocity of movement in a given direction is quite slow and depends upon the time of residence and the diffusion coefficient. This latter is in turn dependent upon the particle size, the smaller the radius the higher the rate of diffusion and the greater the probability of reaching and adhering to the air passage of diameter a . This process of deposition is very important in the alveolar region where the air stream velocities are so low (or zero).

Knowing the parameters which are important in these four processes and using the tube dimensions, velocities, etc. which have been discussed one can roughly determine in which part of the respiratory tract a uniform particulate would deposit. It is clear that impaction is the most important process in the upper part of the respiratory tract and that Brownian motion and sedimentation are controlling factors in the lower part of the lung. Interception can take place most anywhere depending upon the size of the particle and the passage within which it is contained. Figure 5 shows the calculated respiratory tract deposition as a function of particle size, assuming that unit density spheres are being inspired.⁽⁸⁾ Note that upper respiratory deposition is practically zero with 1 micron particles, but can be 60-80% when the diameter approaches 6 microns. The reason for this is that larger particles are more readily thrown from the air stream by impaction and that interception will remove considerable quantities of the real large particulates. Those particles which successfully penetrate the larger bronchi follow a reverse pattern and when the particle size approaches 1 micron the amount which is deposited in the lower respiratory tract rises rapidly. Although these are calculated curves they are representative of many experimental data. The smallest particle shown here is 0.06 microns and is shown to deposit mainly in the alveolar sacs. However these curves represent only that

material which leaves the trachea and it should be understood that as particles get extremely small, their diffusion velocities get to be high and a large fraction deposits in the upper respiratory tract and never reach the trachea.

The preceding graph dealt with spherical particles of unit density and represents an atypical and ideal situation. Particles in general are not spherical, they do not have easily calculated terminal settling velocities and they are often of varied chemical composition. Davies has presented some interesting calculations regarding the pattern of settling as a function of shape.⁽⁹⁾ Figure 6, for instance, shows how triangular, very thin particles (essentially planar) would fall depending upon the angles involved. If isosceles and one angle is less than 60 degrees it will fall with the base downward. If two angles are less than 60 degrees it will settle with the peak downward. If the triangle is not isosceles it is apt to fall most any way depending upon its characteristics. With three dimensional objects, as shown in the lower portion of Figure 6, they tend to orient with the thinnest portion in the vertical position. These examples naturally ignore any outside influences such as air currents but they do indicate how the shape of the particle could play an important role in deposition, particularly in the process of sedimentation.

As examples of the above, Figures 7 - 11 show a few heterogeneous aerosols as seen by the electron microscope. These were generated and photographed in the Aerosol Physics Department at Lovelace Foundation and are shown to indicate how aerosols may resemble some of the shapes shown in Figure 6. Figure 7 is some insoluble montmorellinite clay spheres; this is somewhat an ideal aerosol but still indicates considerable clumping. It would not be easy to calculate the aerodynamic properties of some of these clusters of 4, 5 and 6 spheres and even more difficult to predict their place of deposition in the respiratory tract. The next electron micrograph is from a NaCl aerosol and shows how it forms elegant cuboidal particles. For any given cube it should be possible to calculate its aerodynamic properties. Figures 9 and 10 present ruthenium oxide data and a rather inhomogeneous mixture of sizes and shapes is noted. Figure 9 shows some rods, some blobs and combinations of particles into odd formations. The one particle in the center of Figure 10 is extremely unique. It is not easy to imagine just what type of crystalline form this is. Also, the rings of small dots which surround the crystals are of unknown origin. The last electron micrograph is of a magnesium oxide aerosol and is shown to indicate just how bad the situation could get. There are big cubes and strings of small cubes and attempting to fix a density for any one part of this electron micrograph would be extremely difficult.

Having shown how aerosols can vary in character and having shown how ideal it would be if they didn't vary, it now seems pertinent to discuss what probably is one of the most important parameters involved in estimating where a given particulate may deposit within the respiratory tract. This parameter deals with the hygroscopicity of the aerosol. The humidity of the respiratory tract is extremely high and at the pharynx and the larynx it reaches approximately 99.5% relative. Obviously, if a dry hygroscopic particle were inhaled it would increase in size considerably in traversing the respiratory tract. Therefore, site of deposition may be difficult to predict. As an indication of this Figures 12 and 13 show the deposition pattern of coal dust and NaCl. These figures were copied from Hatch and Gross⁽¹⁰⁾ but are from the original data of Dautrebande and Walkenhorst.⁽¹¹⁾ Figure 12 shows the deposition pattern of NaCl as a function of the particle as it was measured in the dry state. There is no available method of measuring particles in a saturated (wet) state which leads to completely erroneous comparisons of deposition versus particle size for hygroscopic particles. This is very well demonstrated in Figure 13 in which the same NaCl data have been corrected for the size increase which must take place during passage through the respiratory tract. Note the similarity in the two cases. This effect of hygroscopicity upon deposition is extremely important and certainly is an area for continued future research.

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Fig. 1 Anatomical Cross-section of the Human Nasal-pharyngeal Region

Fig. 2 Anatomical View of the Lower Respiratory Tract

Fig. 3 Exploded View of a Typical Lung Lobule, Including the Smaller Bronchi and Alveolar Sacs.

Table 1

MODEL of the RESPIRATORY TRACT

<u>PART OF LUNG</u>	<u>BRANCHING FACTOR</u>	<u>NUMBER</u>	<u>INSIDE DIAMETER, cm</u>	<u>LENGTH cm</u>
TRACHEA	1	1	1.3	11.0
MAIN BRONCHI	2	2	0.85	6.5
FIRST ORDER BRONCHI	6	12	0.4	3.0
2nd ORDER BRONCHI	8	100	0.2	1.5
3rd ORDER BRONCHI	8	770	0.15	0.5
TERMINAL BRONCHI	70	5.4×10^4	0.06	0.3
RESPIRATORY BRONCHIOLES	2	1.1×10^5	0.05	0.15
ALVEOLAR DUCTS	240	2.6×10^7	0.02	0.02
ALVEOLAR SACS	2	5.2×10^7	0.03	0.03

RESPIRATORY CHANNELS OF HUMAN LUNG

Fig. 4

IMPACTION

$$P = f\left(mz, \frac{u}{a}\right)$$

INTERCEPTION

$$P = f\left(d, \frac{l}{a}\right)$$

SEDIMENTATION

$$P = f\left(mz, \frac{t}{a}\right)$$

BROWNIAN MOTION

$$P = f\left(\frac{l}{d}, \frac{t}{a^2}\right)$$

Table 2 Factors Which Effect the Probability, P, of Particulate Deposition in the Respiratory Tract.

Fig. 6 Orientation of Various Shaped Particles in Falling Through a Non-turbulent Atmosphere.

Fig. 7 Electron Micrograph of Montmorellinite Clay Particles

Fig. 8 Electron Micrograph of a Sodium Chloride Aerosol

Fig. 9 Electron Micrograph of a Ruthenium Oxide Aerosol

Fig. 10 Electron Micrograph of a Ruthenium Oxide Aerosol

Fig. 11 Electron Micrograph of a Magnesium Oxide Aerosol

Fig. 12 Deposition of Coal Dust and Sodium Chloride as a Function of Particle Diameter as Collected in the Dry State.

Fig. 13 Deposition of Coal Dust and Sodium Chloride When the Latter Particles Have Been Corrected for Uptake of Water in the Respiratory Tract.

WHOLE BODY DEPOSITION OF PARTICLES AS A FUNCTION OF VARIOUS PHYSICAL AND CHEMICAL PARAMETERS

by Randi Lie

This paper will acquaint the reader with some of the experimental efforts directed toward better understanding of the behavior of particulates in inspired air. Three areas of interest concerning particles are size, density and hygroscopicity, because of the influence they exert upon respiratory deposition. An individual's respiratory pattern also influences the fate of inhaled particles.

Many of the available data which relate to deposition are from studies with humans. The most usual methods of measuring deposition are indirect in which one uses some combination of valves and impingers or impactors. With these methods the amount of an aerosol inspired and the amount expired is measured and the two values are compared.

Both density and hygroscopicity have been dealt with by Landahl and Tracewell⁽¹⁾. They studied the penetration of air-borne particulates through the human nasal passages using several different materials including the following: bismuth subcarbonate, chosen for its high density of nearly 7; corn oil, for its low density; glycerol, a hygroscopic liquid with density 1.3, only slightly greater than that of corn oil. They reported the diameters of particles corresponding to 50% penetration through the nose and found a ratio of less than 2 between bismuth subcarbonate and glycerol. They also introduced the concept of "equivalent impaction diameter," which is defined as the diameter of a sphere of unit density having the same impaction parameters as the particle in question. They felt that if the nasal penetration data were plotted against equivalent diameter they would follow a similar pattern unless some other property was dominating. Figure 1 shows these data. The bismuth subcarbonate data are represented by the letter B, corn oil by O and glycerol by G. Other compounds which are included in the graph are N-sodium bicarbonate, C-calcium triphosphate, M-methylene blue, T-tyrosine and S-sodium sulfate. It can be seen that the values for glycerol are, on the average, lower than any others. This can be attributed to hygroscopicity since the material of similar density, corn oil, shows higher values for penetration at any given particle size.

The influence of particle size upon deposition has been demonstrated by a number of investigators. The pattern of deposition does indeed follow that prescribed in the paper presented by Thomas⁽²⁾. Figure 2 is the work of Brown⁽³⁾, and shows what is thought of as the "classical" deposition curve for the total respiratory system. Minimum deposition occurs at the particle size upon which the 4 physical parameters mentioned in the previous paper (impaction, settling, interception, and diffusion) have the least combined influence. Figure 3 presents data from studies in our laboratory upon deposition of cesium chloride in the rat. In this instance, very small particle sizes could not be obtained and this does not demonstrate a minimum deposition and subsequent increase with smaller particles. It is evident, however, that total deposition does increase with larger particles.

Data of Wilson and LaMer⁽⁴⁾ are given in Figure 4. Total retention is plotted against particle size and the trend towards increased deposition with increased particle size is clear. In addition, it is shown that this trend exists independently of the breathing rate which was varied from 5 1/2 to 20 breaths per minute. The same data plotted differently are shown in Figure 5. It is seen that deposition of any given size particle is considerably lessened by increasing the breathing rate. This can be explained on the basis of quick respirations tending to be shallow and therefore, particles are not drawn to the depths of the respiratory tract. Also, the time of residence of any particle in the respiratory tract is brief under these circumstances.

This being true, it should be possible to show that the greater the volume breathed per inspiration, the greater would be the deposition. Figure 6 is comprised of data of Dautrebande⁽⁵⁾. The upper curve, which shows greater deposition of coal dust at varying particle sizes, corresponds to a tidal volume of 2950 cc. The lower curve relates to a volume of 1950 cc per breath. The respiratory rate was the same in both cases, three breaths per minute. Figure 7, also taken from the work of Dautrebande, shows the effect of changing both tidal volume and respiratory frequency. The largest minute volume corresponds to the least total deposition at any particle size shown.

Subjects in most experiments on humans are trained to breathe in the particular manner reported. The sort of variation existing even under such conditions is shown in Figure 8⁽⁶⁾. For male subjects the range of retention values is from 33 to 53% with a mean of 41% and a standard deviation of 5.1. It is interesting to note that correlations between the other parameters shown and retention are not significant. One

Penetration of Air-borne Particulates Through
the Human Nasal Passages.

Figure 1

Regional Deposition of Inhaled Aerosol in Relation to Particle Size.

Figure 2

Initial Total Deposition of Inhaled Cesium Chloride in the Rat.

Figure 3

Figure 4

Total aerosol retention versus breathing rate. Mouth breathing

Figure 5

Deposition of coal dust particles in the lungs taken as a whole, for a respiratory rate of 3 per minute, according to the tidal volume and given particle sizes

Figure 6

Deposition of Coal Dust Particles in the Lungs Taken as a Whole, According to Tidal Volume, Respiratory Rate and Particle Size.

Figure 7

*Variability in Retention of Small Particles (0.25 μ) of Triphenyl Phosphate
in the Human Lung (12 Second Cycle, 1,350 CC. Tidal Air, 300 CC. Sec.)*

Male Subject	Age	Vital Capacity, L.	Height, In.	Weight, Lb.	% Retained
1.....	37	4.1	71	165	39
2.....	27	5.0	71	160	43
3.....	25	4.2	70	155	53
4.....	32	3.4	65	120	47
5.....	26	4.1	70	155	41
6.....	29	5.4	73	155	48
7.....	26	3.5	66	140	45
8.....	28	5.5	72	190	37
9.....	22	4.6	70	193	39
10.....	20	4.3	71	144	33
11.....	24	3.9	70	160	40
12.....	39	5.4	70	160	40
13.....	26	3.7	70	150	34
14.....	21	4.1	68	155	42
15.....	49	4.1	71	160	35
16.....	35	4.7	71	153	46
17.....	38	3.8	65½	160	42
18.....	23	4.3	68	145	41
19.....	17	4.9	72	140	43
20.....	36	4.0	72	191	44
21.....	38	4.0	71½	200	32
Average.....	29.4	4.3	69.9	160	41
Standard deviation.....	7.8	0.58	2.15	19	5.1
Female Subject					
1.....	25	3.3	66	120	48
2.....	26	2.9	62	150	47
3.....	21	2.3	64	125	47

Figure 8

wonders how any useful data can be derived from animal experimentation when this degree of variation occurs with humans trained to breathe correctly. Studies have shown, however, that good correlation may be made, not only between experimental animals but between animals and man. Figure 9⁽⁷⁾ gives a comparison between the rabbit and the rat of the mean uranium content of lungs at the time of terminal sacrifice following inhalation. The differences are quite small, especially with the smaller particle size. Figures 10 and 11, from the work of Palm⁽⁸⁾, show comparisons of total retention between monkey and man and between guinea pig and man. The similarities are amazingly close in both instances. Figure 12, data from our own laboratory, might easily be compared with the curve for man shown in Figures 10 and 11, although the aerosol vector as well as species has been varied.

It is an extremely hopeful situation that one finds these close parallels between species. At most it appears that an estimate of human deposition values based upon animal experimentation might be in error by a factor of two. In the future we plan to carry out human inhalation exposures to fission products, with the chance of making even better predictions than are now possible.

Mean Uranium Content of Lungs of Terminally Killed Animals Following Inhalation of Uranium Dioxide Particles.

Figure 9

Total retention vs. particle size. Monkey (compared with curve for man).

Figure 10

Total retention *vs.* particle size. Guinea pig (compared with curve for man).

Figure 11

Initial Total Deposition of Inhaled Particulates in the Rat and Guinea Pig.

Figure 12

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EFFECTIVENESS OF EARLY DTPA TREATMENTS
IN TWO TYPES OF PLUTONIUM EXPOSURES IN HUMANS

by

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ABSTRACT

Two cases of plutonium exposure are reported. Both cases were given prompt DTPA (diethylenetriaminepentaacetic acid) treatments. In Case 1, an employee was sprayed with a plutonium nitrate solution. Plutonium entered his body via ingestion, inhalation, and absorption through small acid burns on the skin. In Case 2, an employee's thumb was pierced by a wire contaminated with plutonium oxide. The plutonium levels in their urine, feces, and blood were measured regularly. The effectiveness of the DTPA treatments was markedly different in the two cases.

The DTPA was very successful in removing the soluble plutonium in Case 1. In Case 2, however, the effectiveness of the treatment was inconclusive.

INTRODUCTION

Animal studies¹⁻⁷ have shown that DTPA (diethylenetriaminepentaacetic acid) is presently the most effective chelating agent for accelerating the excretion of plutonium from biological systems. These studies have shown that the effectiveness of the DTPA treatment depends on (1) the chemical form of the plutonium, (2) the mode of entry of the plutonium into the body, (3) the promptness of the treatment, and (4) the amount and method of administration of the DTPA. Norwood⁸⁻¹¹ has reported the results of DTPA treatments on six humans who had been previously exposed to plutonium via inhalation. He demonstrated that 1-gram quantities of DTPA administered intravenously by slow drip was the most effective treatment. He also reported the effect of early DTPA treatment on a plutonium-contaminated wound.¹²

In the two cases reported here, the DTPA treatments were administered within 1 hour of the accident by Dr. S. V. Guzak.

CASE 1

Description of Accident and Treatment

In October, 1963, a laboratory technician at Rocky Flats was involved in an accident with an acidified solution of PuCl_3 , PuCl_4 , and $\text{Pu}(\text{NO}_3)_4$. A plastic level gauge was broken and the employee was sprayed with the acid solution. The solution contained (by alpha activity) 70% Pu^{239} , 14% Pu^{240} , and 16% Am^{241} . He was contaminated over most of his body with from 10,000 to 50,000 d/m per 67 cm^2 . Several small areas on the face were greater than 500,000 d/m per 67 cm^2 . These areas were found to be small second-degree burns containing nearly 5 ug of plutonium. His body, except for the burns, was successfully decontaminated with a dilute solution of sodium hypochlorite. After 2 weeks the scabs were removed from the burns and found to contain the plutonium. The areas under the scabs were less than minimum detectable amounts (0.004 ug) when measured with the Rocky Flats Wound Counter.¹³ DTPA treatments were started within one hour of the accident and repeated 5 hours later. Two treatments were also given on the 2nd and 3rd days after the accident. On the 4th, 5th, 13th, 15th, and 17th days, one treatment was given. In each treatment, 1 gram of DTPA was given intravenously in 250 cc. of saline solution.

Results and Discussion

A continuous sampling program was initiated to determine the amounts of plutonium in the urine, feces, and blood. The fecal, blood, and urine sample results are shown in Tables I, II, and III. The urine sample results are shown on a semilogarithmic plot in Figure 1. This employee (Case 1) had an average 24-hour urine excretion of 0.31 d/m plutonium for 9 months prior to this accident. This amount was subtracted from each sample result in Figure 1. A least squares fit of this data for days 1-5 and for days 6-47 yields half-lives of 1 and 6 days, respectively, for elimination.

Fifty days after the accident, urine levels had decreased to nearly the same as the pre-accident level (0.31 d/m/24 hrs.).

Table I

Case 1 Plutonium in Feces

<u>Days after</u> <u>Accident</u>	<u>D/m/24 hrs.</u>
0	13,600
2	3,100
3	660
4	350
5	376
7	101
15	16.7
16	23.9
18	27.4
25	16.3

Table II
Case 1
Plutonium in Blood

<u>Days after Accident</u>	<u>D/m/6000 ml.</u>
0	1,550
1	780
2	900
3	336
4	186
6	96
8	124
12	104
14	36
16	186
21	150
28	52
42	39

Table III
Case 1
Plutonium in Urine

<u>Days after Accident</u>	<u>D/m/24 hrs.</u>	<u>Days after Accident</u>	<u>D/m/24 hrs.</u>
0	2,586.	33	0.79
1	812	34	0.53
2	287	35	1.25
3	196.	36	1.50
4	105.	37	1.43
5	48.3	40	1.49
6	27.9	41	1.08
7	35.8	42	1.06
8	38.3	43	0.68
9	22.6	44	0.56
12	27.1	46	0.65
13	15.9	47	0.59
14	17.1	48	0.31
15	12.8	50	0.37
16	5.1	51	0.48
18	5.7	56	0.10
19	3.4	65	0.58
20	5.1	71	0.14
21	4.3	78	0.38
22	1.1	92	0.37
23	1.0	99	0.50
25	4.6	135	< 0.10
26	2.0	156	0.17
27	3.4	201	0.30
28	2.5	245	0.10
32	1.2	261	< 0.10

CASE 2

Description of Accident and Treatment

In December, 1963, an employee working in the plutonium fabrication area suffered a puncture wound from a wire contaminated with PuO_2 . The wire passed completely through his thumb in the soft tissue just above the first knuckle. He was taken to the medical department where the wire was removed. The wire was assayed and found to contain 2.3 μg of plutonium. A wound count was made using the Rocky Flats Wound Counter. Nearly 1.8 μg of plutonium were found to be in the wound. DTPA treatments were started within 1 hour of the accident and repeated on the 1st, 3rd, 4th, 7th, 9th, 11th, 14th, 16th, and 18th days following the accident. One-gram quantities were administered intravenously by slow drip. On the 4th day, two excisions were made on the thumb. One was made on the side where the wire entered and the other was made where the wire emerged. The excised tissue was assayed and found to contain 0.730 μg of plutonium. Nearly all of this (0.715 μg) came from the side where the wire had entered.

Wound counts were made at regular intervals over the next 6 months. Each recount was higher than the previous one, indicating that the remaining plutonium was moving toward the surface. At the same time, it became apparent that several small nodules were forming at the wound site. On July 22, 1964, these nodules were removed. A total of 0.80 μg was found in the removed tissue. A recount of the thumb 1 week after surgery indicated that 0.28 μg remained.

Results and Discussion

A program was initiated immediately to determine the amount of plutonium in the blood, urine, and feces. Since the accident occurred at 2:30 p.m., 24-hour samples were taken from 2:30 p.m. to 2:30 p.m. Blood samples were taken at 9:00 a.m. When DTPA treatments were given, the blood samples were taken just prior to the treatment. The total amount of plutonium in the blood was determined from 30-ml samples and an assumed 6000-ml. blood volume. The results of the sampling program are shown in Table IV.

The urine and blood results for the first 28 days are also shown on a semilogarithmic plot in Figure 2. This plot shows that the amount of plutonium excreted in the urine by 2:30 p.m. totals about the same as was present in the blood prior to the DTPA treatment that morning.

We suggest that the following may have been involved in this case:

1. The plutonium present in the blood prior to DTPA treatment was rapidly removed via the urine after treatment.
2. The plutonium levels in the blood experienced a sharp drop after DTPA treatment followed by a slow increase to the pretreatment levels.
3. The transfer of plutonium from the wound to the blood remained at a fairly low rate during this period.

In a more recent case involving insoluble plutonium, the rapid drop of plutonium levels in the blood has been verified. It was shown by taking blood samples prior to, just following, and several hours after the DTPA treatment. The justification for assuming a slow transfer of plutonium to the blood rests on the observation that if this were not so, the amount excreted in the urine would exceed the amount present in the blood prior to the treatment. In another recent case involving soluble plutonium, the amount excreted in the urine exceeded the amount present in the blood by factors as large as 10.

The total excretion over the first 20 days amounted to 16% of a maximum permissible body burden. Presumably a good share of this would have remained in the body had DTPA not been administered. There is no way of knowing, however, what effect the DTPA had on increasing the transfer of plutonium from the wound to the blood. The overall effects of the DTPA treatments are therefore not conclusive.

A systemic body burden has not been estimated in this case. The uncertainties involved in relating urine excretion to body burdens in wound cases has been previously pointed out by Hammond.¹³

Table IV
Case 2
Plutonium in Urine, Blood, and Feces

<u>Days after Accident</u>	<u>Urine d/m/24 hrs.</u>	<u>Blood d/m/6000 ml.</u>	<u>Feces d/m/24 hrs.</u>
0		879	1.0
1	2784.	3429.	2.8
2	1055.		
3	741.	2721.	
4	1637.	3696.	11.2
5	190.		
6	40.		
7	2290.	3570.	46.1
8	44.		67.0
9	810.	1980.	11.4
10	274.		97.0
11	2416.	1590.	82.2
12	380.		76.3
13	410.		63.7
14	392.	1380.	110.3
15	599.		104.3
16	293.	846.	51.6
17	231.		41.7
18	944.	1149.	102.2
19	95.		96.6
20			21.5
21	295.	828.	3.0
22	43.		
23	39.		27.8
24	122.		53.1
25	54.		
28	89.		42.3
29	3.2		
30			19.0
35			15.5
42		750.	
43			48.3
58	19.6		
64	5.7		
71		1100.	
80	15.7		
98		420.	
109	8.2		
136	4.2		
165	2.7		
204			1.9
205	7.0	480.	
205 (after surgery)		112.	
206	4.3		
207			2.9

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Figure 1
(Case 1)

Disintegrations per Minute
in a 24-hour Urine Sample

The Interpretation of Analytical Results
for Radionuclides in Urine

by

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Abstract

A brief summary is presented of the human data available on metabolism and excretion of caesium, phosphorus, plutonium, polonium, radiation, strontium, sulphur, tritium and uranium.

Following a recognised accidental intake of a radionuclide, it is desirable to analyse a carefully planned series of urine samples, to provide a measure of the excretion rate of the individual and to minimise the uncertainty associated with single, isolated results.

For assessment of routine urine analysis results from a group of personnel, the excretion data can be used to calculate the urinary concentration related to a chosen level of body content at which further investigation is required. Routine results should be carefully recorded for use in periodical reviews of their long-term significance.

1. Introduction

The most accurate method of measuring the body content for those radionuclides which emit penetrating X- or gamma-radiation, e.g. caesium-137, radium-226, or Bremsstrahlung e.g. phosphorus-32, strontium-90, is by means of a whole body activity measuring facility⁽¹⁾⁽²⁾. For the estimation of body content of those radionuclides which only emit soft radiation e.g. plutonium-239, tritium, it is necessary to depend on bio-assay, i.e. analysis of specimens of tissue or excreta for their radionuclide content. Because it only requires rather simple equipment, bio-assay is often used for radionuclides which could be measured directly in vivo. If sufficient information is available about the metabolism, distribution and excretion of a radionuclide, it is possible to deduce from bio-assay results the amount of radionuclide retained in the body, and the consequent radiation dose. Radionuclides may enter the plasma or interstitial fluids by absorption from the GI tract or the lungs, or through a wound. Some of the radionuclide may then be preferentially retained in one or more organs such as the liver, thyroid or bones, making the radiation dose to a particular organ the critical consideration. Absorption of a substance from the GI tract is small in the absence of a specific process of active transport.

In dealing with internal contamination of the body resulting from inhalation of radionuclides it is common practice to consider different compounds under the two categories 'soluble' and 'insoluble'. It is important to note that the relevant consideration is the degree of solubility of a compound in body fluids, which may be different from its solubility in non-physiological fluids. An important example of this is plutonium nitrate, which, although freely soluble in acid, is hydrolyzed to the insoluble hydrated oxide at physiological (neutral) pH. On the other hand, strontium carbonate, which is almost completely insoluble in water, has been shown to be rapidly absorbed from the lung into the body fluids⁽³⁾. A generalised description of the metabolism, distribution and excretion of a radionuclide can only apply to those chemical compounds which are rapidly and completely absorbed and subsequently transported round the body in the same chemical form.

The ready availability of urine makes it the most important material for bio-assay. In a normal man, about 170 litres of fluid per day is filtered from the plasma through the glomeruli of the kidney. In the tubules selective resorption of certain substances which have passed through the glomeruli occurs by specific active transport mechanisms. Other substances are specifically secreted through the kidney tubules into the urine. Almost all the water filtered through the

glomeruli is resorbed in the tubules, only about 1.4 litres per day being excreted as urine⁽⁴⁾. The relationship between the concentrations of a soluble substance in the urine and in the plasma depends specifically on its extent of secretion or resorption in the tubules.

There is a small amount of published data available about the urinary excretion resulting from the inhalation of radionuclide compounds which are only slightly soluble in body fluids, e.g. radium sulphate⁽⁵⁾, uranium oxide⁽⁶⁾⁽⁷⁾, strontium carbonate⁽³⁾ and plutonium oxide^{(7) (8) & (9)}. Among these cases there is a wide variation in the relationship between the urinary excretion rate and the body content.

2. Interpretation of urine analysis measurements for individual cases, following a single intake of radionuclide

Calculation of the radiation dose delivered to the critical organ depends on a knowledge of the distribution of the radionuclide in the body and in particular the fraction which is located in the critical organ. For most radionuclides, the relationship between urinary excretion rate and body content is deduced from a small number of case histories of human metabolism. When investigating an accidental intake a series of urine samples should be analysed, to reduce the margin of uncertainty attaching to individual results, and to permit comparison of the trend in excretion rate with that in the reference cases. There is urgent need for more data which would be obtained best from controlled human experiments in cases where such experiments would only involve commitment to a very small radiation dose.

In the case of long-lived, bone-seeking radionuclides e.g. plutonium-239, strontium-90, the dose-rate to bone is almost constant, because of the extremely slow turnover of such radionuclides in bone, and the total dose to bone is therefore a simple multiple of the dose rate. Because of the rapid clearance of other tissues, the bone content of radionuclide soon becomes virtually the total body content, which is therefore commonly used as the most convenient index of the radiation dose in the case of these long-lived bone-seekers.

3. Urine analysis in the routine surveillance of groups of radiation workers

In contrast to the concern with precision in the case of individual investigations, routine urine analysis is primarily intended as a screening process, designed to detect any occurrence of significant intake of a radionuclide which has otherwise escaped attention. For this purpose, it is convenient to use the available metabolic data to define a level of urinary excretion rate of radionuclide below which there is no need for further enquiry, but above which an investigation of the circumstances is required; this level is stipulated as the investigation level.

The Investigation Level is often chosen to correspond to a body content of 1/10th of the maximum permissible body burden (MPBB) recommended by ICRP (1959)⁽⁴⁾. In the case of radionuclides with a short effective life in the body, e.g. phosphorus-32, it may be feasible to relax the investigation level to correspond to an intake of one-tenth of the maximum permissible amount⁽⁴⁾. In the case of bone-seeking radionuclides with a long effective life-time in the body, the long-term urinary excretion rate does not follow an exponential law but is more satisfactorily represented by a power law. In consequence, there is not a constant relationship between the urinary excretion rate and the body content, even after a single isolated intake. This relationship becomes still more difficult to define if more than one intake has occurred. Hence, it is not sufficient to compare each urine analysis result with a constant value for the investigation level; the choice of investigation level for these radionuclides is a complex problem⁽¹⁰⁾.

The frequency with which routine samples are taken depends on the degree of confidence in the measurement and control of the environment, and on the effective life-time of the radionuclide in the body.

4. Practical considerations in the determination of radionuclides in urine

In general, efficient analytical techniques have been developed for the determination of very small amounts of radionuclides in urine⁽¹¹⁾.

There are considerable day to day fluctuations in the urinary excretion rate of bone-seeking radionuclides, e.g. plutonium-239⁽¹²⁾, strontium-90⁽¹³⁾. The most economical way of establishing the mean urinary excretion rate would be to measure an aliquot of the combined urine samples collected over a period of several days, rather than to make separate measurements on a number of daily samples. If urine specimens are combined, or indeed whenever there is any uncertainty about the metabolic period represented by a urine sample, it is convenient to use the creatinine content as an internal standard. The rate of creatinine excretion by individual people is remarkably constant, and the variation between people is not very great. If individual creatinine excretion rates have not been measured, average values of 1.7g per day for men and 1.0g per day for women will give a sample time accurate to within a factor of 0.5 to 1.5 in 95 per cent of cases⁽¹⁴⁾.

5. Evaluation of the urinary investigation level from the available metabolic data

5.1 Caesium-137

About ten per cent of this radionuclide is rapidly excreted (biological half-time about 1 day) and the rest is turned over much more slowly (biological half-time 50-150 days, mean about 110 days). About 90 per cent of the caesium-137 excreted is

found in the urine⁽¹⁵⁾⁽¹⁶⁾. These values lead to the equation given in Fig. 1 for the rate of urinary excretion of caesium-137. Approximately 10 days after intake the daily urinary excretion rate becomes 0.6 per cent of the body content at the time of excretion. The maximum permissible body burden of caesium-137 is 30 μc so that the urinary investigation level corresponding to one-tenth of this is 0.018 μc per day, rounded to 0.02 μc per day (radioactive decay is negligible - the physical half-life of caesium-137 is 11,000 days).

5.2 Phosphorus-32

About 30 per cent of phosphorus-32 entering the bloodstream as soluble inorganic phosphate is rapidly deposited in bone⁽¹⁷⁾, where it is turned over at a rate negligible by comparison with the radioactive decay (physical half-life 14.3 days). Another 30 per cent is rapidly excreted⁽¹⁸⁾⁽¹⁹⁾, and the remaining 40 per cent is initially deposited in soft tissues and eventually excreted after a biological half-time of about 19 days⁽²⁰⁾. Excretion is very largely in the urine; the equation presented and graphed in Fig. 2 has been fitted to the available results on urinary excretion which after the sixth day, are only available for one intake by one person⁽²¹⁾.

With bone critical, the maximum permissible single intake to blood via inhalation or ingestion is 27.5 μc of phosphorus-32⁽²¹⁾. The daily urinary excretion rate after 14 days is 0.9 per cent of the intake to blood; because one physical half-life has elapsed, this is 0.45 per cent of the initial intake when the quantities are expressed in units of radioactivity. The investigation level may be taken as $\left(\frac{27.5}{10} \times \frac{0.45}{100}\right) \mu\text{c}$ per day = 12 m μc per day for sampling at intervals of 14 days.

The organic phosphorus compound DFP(di-isopropylfluorophosphonate) is well-known to attach itself to red cells, and phosphorus-32 administered in this form is not deposited in bone to any significant extent; the critical organ is total body, and the maximum permissible single intake to blood is five times as high as when bone is critical. The urinary excretion rate follows a similar course to that of soluble inorganic phosphate, so in this particular case an investigation level 5 times as high would be acceptable⁽²¹⁾. However, it is not permissible to apply this relaxation to any other compound unless there is equally clear evidence that bone deposition is negligible.

It should be borne in mind that phosphorus is an essential constituent of nucleic acids, and that disintegration of phosphorus-32 incorporated in DNA may have direct genetic effects. It is exceedingly difficult to determine whether these are comparable in magnitude to those caused by the general irradiation resulting from the presence of phosphorus-32 in the body as a whole⁽²²⁾.

5.3 Plutonium-239

Langham's classical data on human metabolism of plutonium⁽²³⁾ were obtained

from studies in which plutonium citrate was injected intravenously. The equation deduced for the urinary excretion rate was $U(t) = 0.23t^{-0.77}$. Because most other plutonium compounds are only slowly absorbed from the lung or from wounds, the application of Langham's results to the interpretation of plutonium excretion arising from accidents is difficult and complicated. Beach and Dolphin⁽¹²⁾ have predicted urinary excretion rates from reasonable assumptions about the rate of absorption of plutonium from the site of entry to the body; some of the results of their calculations are illustrated in Fig. 3. Although initially the excretion rate is strongly dependent on the rate of absorption this is no longer the case after a year or so. A more satisfactory estimate of the body content of plutonium should therefore be possible when a time of this order has elapsed since the accidental intake.

The investigation level is particularly difficult to choose for plutonium, and although the curves in Fig. 3 are helpful it must be remembered that they are not directly founded on experimental data. A value of 0.4 μC of plutonium-239 in the urine per day has been used provisionally pending further consideration of the problem⁽¹⁰⁾.

Plutonium oxide is absorbed very slowly from the lung, but Dolphin has suggested that the consequent long-term urinary excretion rate may be related to the total amount of plutonium in the body, including the lung in this case⁽²⁴⁾. More information is required to test the validity of this hypothesis.

5.4 Polonium-210

Polonium appears to be excreted from the body in a simple exponential manner apart from an initial slower phase in the case of inhalation of insoluble material. The proportions excreted in urine and faeces are somewhat variable⁽²⁵⁾⁽²⁶⁾; here, the urinary excretion is taken to be 10 per cent of the total, with an overall biological half-time of 50 days (Fig. 4). The urinary excretion rate is thus 0.14 per cent of the body content at the time of excretion. The daily excretion corresponding to one-tenth of the maximum permissible body burden, viz. 0.03 μC (spleen critical) is $\left(\frac{0.03}{10} \times \frac{0.14}{100}\right) \mu\text{C} = 4 \text{ pC}$. This value for the investigation level may be relaxed for sampling intervals less than 60 days, which is the time required for the maximum permissible single intake of 0.1 μC to fall to the maximum permissible body burden (effective half-life 37 days, taking into account radioactive decay as well as excretion⁽²⁶⁾).

5.5 Radium-226

Comparatively little attention has been paid to the excretion of radium in urine and faeces. Human body content of radium-226 has usually been determined from measurements of radon-222 in breath or direct measurements of radium-C (bismuth-

214) in the body. However, the equation in Fig. 5 is a satisfactory representation of results from three different studies⁽²⁷⁾⁽²⁸⁾⁽²⁹⁾ the major variability being the distribution of excreted radium between urine and faeces. A value of 2 per cent in urine has been taken as being most representative of the very wide range observed (0.3 per cent to 17 per cent⁽³⁰⁾).

It is not possible to specify a unique value of investigation level for radium in urine because the excretion rate is not exponential. For a 3-monthly sampling programme, a level of 1 pc of radium-226 in urine per day ensures that not more than 0.01 μ c (one tenth of the maximum permissible body burden - bone critical) is present in the body, but it should be noted that up to one-fifth of the maximum permissible dose may have been received by the bone during the previous 13 weeks.

5.6 Strontium-90

Human metabolism of strontium has been reviewed by Dolphin and Eve⁽³¹⁾⁽³²⁾ who described the retention and excretion as the sum of an exponential term and a power-law term (Fig. 6). Radioactive decay can be neglected because of the very long physical half-life. Half of the strontium-90 entering the bloodstream is rapidly excreted (biological half-time 2.4 days); the other half is deposited in bone and then turned over very slowly. About 80 per cent of the excretion is in the urine.

Because the excretion rate is not a simple exponential fraction of the body content, it is essential to know the time of an intake in order to estimate its magnitude from excretion data. Likewise, the value taken for the investigation level is dependent on the frequency of routine sampling. For a 3-monthly sampling programme, a level of 400 pc of strontium-90 per day in urine corresponds to a body content at the time of sampling of 0.2 μ c (one-tenth of the maximum permissible body burden, with bone as the critical organ). If this is the consequence of an intake at the beginning of the preceding 13 weeks, one-seventh of the maximum permissible dose for that period will have been received by the bone.

5.7 Sulphur-35

Sulphur-35 injected intravenously in the form of soluble, inorganic sulphate penetrates very slowly into cells, and urinary excretion is rapid in the early stages; the mean half-life observed in 5 normal subjects was 5-9 hours⁽³³⁾. Data for urinary excretion at later stages are confined to one patient suffering from chondrosarcoma (malignancy in cartilage); it is difficult to judge whether this affected his metabolism of sulphate⁽³⁴⁾. The equation in Fig. 7, which is deduced from these data, available for a period of 10 days after injection, consists of two

exponential terms, which probably represent turnover in extracellular and intracellular fluid respectively. The first term covering the early rapid excretion, is dominant for 1-2 days; subsequently, the second term is dominant, the biological half-time is 7 days and hence 10 per cent of the body content is excreted per day in the urine.

I.C.R.P. Committee II (1959)⁽⁴⁾ takes testis as the critical organ for sulphur-32, but this is based on a value of 4 per cent for the sulphur content of testis, which is not borne out by recent analytical results⁽³⁵⁾. It seems more realistic to take the whole body as the critical organ, with 400 μ c as the maximum permissible body burden, giving an investigation level of 4 μ c of sulphur-35 in urine per day (correction for radioactive decay is not important, because the physical half-life is 87 days).

The metabolism of organic compounds of sulphur-35 may be very different from that of inorganic sulphate. In particular, sulphur in the amino-acids cysteine and methionine will enter the organic sulphur pool and may be retained more persistently in the body.

5.8 Tritium

Tritium gas is not readily retained in the body in significant amounts⁽³⁶⁾, but tritiated water mixes with the water of the body rapidly and completely. Tritiated water may enter the body by ingestion, inhalation or absorption of liquid or vapour through the skin. Under normal conditions of fluid intake the concentration of tritiated water is the same in urine as in body water, and excretion therefore follows a simple exponential equation (with the exception of a small fraction which is retained for a much longer period after incorporation in organic compounds⁽³⁶⁾). The mean biological half-time is about 9.5 days⁽³⁷⁾⁽³⁸⁾ but individual values may be as high as 18 days⁽³⁷⁾.

ICRP Committee II (1958) has adopted a value of 12 days⁽⁴⁾, with 60 per cent of the excreted tritium in the urine; hence, the urinary excretion rate expressed as a proportion of the body content at the time of excretion is 3.5 per cent per day (Fig. 8). The maximum permissible body burden (body tissue critical) is 1,000 μ c, and the urinary investigation level corresponding to one tenth of this is 3.5 μ c per day, or approximately 3 μ c per litre. This is applicable to the long term steady state and is therefore equal to the value of $(MPC)_w$ for continuous exposure⁽⁴⁾.

The maximum permissible single intake of tritiated water is 4,000 μ c and it takes 24 days for this to fall to the maximum permissible body burden. It is therefore possible to relax the investigation level for sampling intervals less than 24 days.

Tritium in organic compounds may be biochemically incorporated in body tissues and then retained more persistently; the best known case is that of tritiated thymidine, which is incorporated in DNA. In such cases, special consideration must be given to the evaluation of the urinary investigation level.

5.9 Uranium

The equation graphed in Fig. 9 represents the results of Bernard and Struxness⁽⁴⁰⁾ for urinary excretion of uranium by terminal brain cancer patients after intravenous injection of soluble uranium compounds. (Comparable results for non-terminal patients were obtained by Bassett et al⁽⁴¹⁾). Two-thirds of the intake was excreted in the urine during the first 24 hours, faecal excretion being negligible. Radioactive decay is also negligible.

With natural uranium, the critical consideration is the non-radiological toxicity to the kidney⁽⁴²⁾. It is appropriate to calculate a urinary investigation level corresponding to $(MPC)_a$ for soluble natural uranium ($210 \mu\text{g per m}^3$) which was deduced from measurements of air concentration in animal tests of the toxic effects of inhaled soluble uranium compounds. The following values were adopted by ICRP Committee II (1959)⁽⁴⁾ for Standard Man:-

Volume of air inhaled during 8 hours work = 10 m^3

Fraction of inhaled soluble particles
retained and absorbed = 25 per cent

Volume of urine excreted daily = 1.4 litres.

Hence, the concentration of natural uranium in urine immediately after inhalation of $(MPC)_a$ throughout one work-shift = $210 \times 10 \times \frac{25}{100} \times \frac{2}{3} \times \frac{1}{1.4} = 250 \mu\text{g per litre}$.

(Extensive experience with uranium workers has shown that albumenuria is never attributable to uranium when there is less than $100 \mu\text{g}$ uranium per litre of urine collected immediately after work⁽⁴³⁾).

In the case of enriched uranium with a specific α -activity greater than $3.3 \mu\text{c/g}$, irradiation of bone is more critical than toxicity to the kidneys⁽⁴²⁾. Bernard and Struxness⁽⁴⁰⁾ concluded that the rate of turnover of uranium in human bone could be represented by a biological half-life of 300 days, in accord with animal data⁽⁴⁴⁾. This is alternatively expressed as a daily excretion rate of 0.23 per cent of the bone content per day (Fig. 9). The maximum permissible body burden for uranium-234 is $0.05 \mu\text{c}$, 85 per cent of which is assumed to be in bone. The urinary investigation level corresponding to one-tenth of this is $10^{-5} \mu\text{c} = 10 \text{ pc per day}$. For a considerable time after an intake of soluble uranium, excretion of uranium released from bone is overshadowed by uranium released more rapidly from other tissues. This implies a greater margin of safety in all cases falling below

the investigation level, both in samples collected after a week-end or even after a holiday. Sampling immediately after work with soluble enriched uranium is not recommended because it is not practicable to estimate the radiological hazard to bone from the urinary excretion rate during the early phase of rapid excretion.

6. Discussion

The possibility of estimating the level of internal contamination of the body from the analysis of urine samples depends on adequate information about the metabolism, distribution and excretion of the radionuclides concerned. The amount of data available is not at present entirely satisfactory for any of the elements. It is urgently necessary to reinforce existing knowledge of radionuclide metabolism; this would be best done by controlled human experiments, wherever this is possible with a permissibly small radiation dose commitment; in cases where this is not possible, properly designed animal experiments are very valuable. No opportunity should be missed of collecting excretion data after accidental intakes, together with measurements of radiation actually emitted from the material retained in the body, if this is feasible. Further useful evidence is obtainable by the analysis of post mortem specimens from persons who have been radiation workers.

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Figure 1 Urinary Excretion of Caesium-137 after a Single Intake

Figure 2 Urinary Excretion of Phosphorus-32 after a Single Intake in the form of Soluble Inorganic Phosphate

Figure 3 Plutonium: Urinary Excretion after an Intake of 0.04uc

Figure 4 Urinary Excretion of Polonium-210 after a Single Intake

Figure 5 Urinary Excretion of Radium-226 after a Single, Soluble Intake

Figure 6 Urinary Excretion of Strontium-90 after a Single Intake

Figure 7 Urinary Excretion of Sulphur-35 after Intake in the Form of Soluble Inorganics

Figure 8 Urinary Excretion of Tritium after a Single Intake in the form of Tritiated Water

Figure 9 Urinary Excretion of Uranium after a Single, Soluble Intake

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DETERMINATION OF PROMETHIUM-147 IN ENVIRONMENTAL SAMPLES

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Abstract

A procedure employing a combination of simple analytical techniques was developed to determine Pm^{147} in environmental samples. Lanthanides were initially precipitated from solution as hydroxides. Rare earths that interfere with beta counting of Pm^{147} and other contaminants were removed by ion exchange, solvent extraction, and precipitation. Pm^{147} was finally co-precipitated with neodymium oxalate, fired to the oxide, and counted in a gas-flow proportional counter. Recovery was $71\% \pm 9\%$ (relative standard deviation). Decontamination factors for fission products usually found in environmental samples were $>10,000$.

Introduction

Promethium-147 is a long-lived fission product which is not a major biological hazard because the fraction of the ingested radionuclide reaching the blood is extremely small. However, recognition of its fate in the environment is important so that still another source of man's exposure to radiation can be better evaluated.

Classical methods based on ion exchange and solvent extraction (1,2) for the determination of Pm^{147} in the presence of other fission products are lengthy, complicated, and often require specialized equipment. These various methods are not readily adaptable for routine analyses of environmental samples.

Portions of several methods (2,3) used to analyze control samples from large-scale fission product recovery processes were modified and combined to provide a simple routine procedure for environmental samples.

Discussion

Several methods (2,3) used to analyze control samples from large-scale fission product recovery processes were modified and combined to provide a simple procedure for environmental samples. The radiochemical determination of Pm^{147} is difficult because it is hard to separate elements of the lanthanide series. Yttrium, scandium, and tripositive actinide elements are chemically similar to the lanthanides and interfere in rare earth analytical procedures. Stable iron, found in many environmental samples, interferes with the determination of Pm^{147} by some procedures.

Pm^{147} has no gamma rays associated with its decay; it must be determined by beta counting. Hydroxide precipitation is an easy and practical method of determining rare earth elements as a group. Promethium has no stable isotope that can be used as a carrier so chemically-similar neodymium was used as a carrier (3). Stable cerium was added to carry Ce^{144} . Rare earth hydroxides that were precipitated from a solution of mixed fission products also carried Y^{90} , Zr^{95} , Ru^{106} , Cs^{137} , and stable iron. See figure 1.

Iron and Zr^{95} were easily removed by absorption as chloride complexes on an anion exchange column. The hydroxide precipitate was dissolved in concentrated hydrochloric acid and passed through a Dowex-1, 100-200 mesh, anion resin column. The column retained <1% of the rare earths but removed 100% of the Zr^{95} and iron.

Britt (2) proposed a method for removing Y^{90} from 1.65M nitric acid solution by extraction with purified 0.75M di-2-ethylhexylphosphoric acid (HDEHP) dissolved in ultrasene. The HDEHP was not purified for our experiments. The solvent extraction step removed all the Y^{90} , Cs^{137} , Ru^{106} , and some Ce^{144} .

All rare earths precipitate as iodates, but cerium (IV) iodate is the only one which is insoluble in strong acid solutions (1). Cerium (III) was oxidized to Ce (IV) with sodium bromate in approximately 5M nitric acid, and then precipitated as the iodate $[\text{Ce}(\text{IO}_3)_4]$. The other rare earth iodates remained in solution. About 30% of the Pm^{147} present was carried on the $\text{Ce}(\text{IO}_3)_4$ precipitate. This accounts for the low but consistent chemical recovery through the procedure.

Rare earth oxalates are only slightly soluble in water, and the oxalate precipitate is easily planchettied and fired to the oxide (1). Pm^{147} was precipitated with neodymium oxalate as a carrier at pH 6-7. Rare earths other than neodymium and Pm^{147} in the solution precipitated but did not interfere in environmental sample analyses because

their fission yield is either very low or their half-life is short. See table 1.

The oxalate precipitate was planchatted, dried, and fired to the oxide. Pm^{147} was counted in a gas-flow proportional counter. Counter efficiency was about 25% for the 0.23 Mev beta energy. Presence of Pm^{147} was verified by recount with a 4.5 mg/cm^2 aluminum absorber which absorbed 55% of the beta.

Recovery and Decontamination Factors

Recovery of Pm^{147} from spiked water solutions and from spikes added to environmental samples (air, rainwater, and seepage basin water) was $71\% \pm 9\%$ (relative standard deviation). Table 2 shows typical recoveries of Pm^{147} . Decontamination factors for fission products usually found in environmental samples were $>10,000$.

Analytical Procedure

Sample Preparation

Air. Particulate fallout was collected on an asbestos-reinforced organic filter. Approximately 27,000 cubic feet of air had passed through each filter. The filter was burned in a muffle oven to remove organic material. The residue was leached with dilute hydrochloric acid and then filtered. The filtrate was analyzed for Pm^{147} .

Rainwater. Radioactive contaminants were removed by passing the rainwater through a mixed bed ion exchange resin column. The radioactive contaminants were desorbed from the column with nitric acid (4). The eluate was diluted to a known volume and a portion of the solution analyzed for Pm^{147} .

Steps of the Analysis

1. Transfer a suitable aliquot of the sample which is in acid solution to a centrifuge tube and add 10 mg each of Nd and Ce carriers.
2. Make the solution basic with NH_4OH and centrifuge the slurry.
3. Dissolve the precipitate in 5 ml of 12N HCl and pass the solution through a Dowex-1 resin (100-200 mesh) column which has been prewashed with 12N HCl. Rinse the column with 10 ml of 12N HCl. Retain all column effluents.
4. Dilute the column effluent to twice its volume with distilled water and add 15 ml of 12N NaOH. Continue the addition of 12N NaOH dropwise until the solution is basic and the precipitate forms. Centrifuge and discard the supernate. Wash the precipitate once with distilled water.
5. Dissolve the precipitate in 10 ml of 1.65N HNO_3 and transfer the solution to a 125 ml separatory funnel. Rinse the centrifuge tube with 1.65N HNO_3 until the volume of the solution is 20 ml. Add 20 ml of 0.75M HDEHP in ultrasene to the separatory funnel and shake for two minutes. Drain the aqueous phase into a centrifuge tube.
6. Add 10 ml of 16N HNO_3 , 2 ml of 1M NaBrO_3 , and 5 ml of 0.7M HIQ_3 to the sample. Heat in a water bath and then cool in an ice bath. Centrifuge and discard the precipitate.
7. Add 2 mg Ce carrier to the supernate and repeat step 6.
8. Add 12N NaOH to the supernate until the solution is basic and the precipitate forms. Centrifuge and discard the supernate.
9. Dissolve the precipitate in a minimum amount of 12N HCl and dilute the solution to about 25 ml with distilled water. Heat to $80^\circ\text{-}90^\circ\text{C}$ and add 10 ml of saturated ammonium oxalate. Adjust the pH to 6-7 with 6N NH_4OH and remove from heat.

10. Allow the sample to cool. Centrifuge and transfer the precipitate to a stainless steel planchet. Dry under a heat lamp and flame to the oxide.
11. Count the sample in a gas-flow proportional counter. Recount with a 4.5 mg/cm^2 aluminum absorber. The absorber should reduce the original corrected count by 55%.

Summary

Promethium-147 and other fission products were precipitated as hydroxides from acid solutions. The hydroxides were converted to chlorides and passed through an anion exchange resin column. Further purification was accomplished by precipitation and solvent extraction. Promethium was finally precipitated with neodymium oxalate as a carrier, fired to the oxide, and counted in a gas-flow proportional counter.

Decontamination factors for common fission products in environmental samples were $>10,000$. Recovery of added Pm^{147} spike was $71\% \pm 9\%$ (relative standard deviation).

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FIGURE 1. DETERMINATION OF PROMETHIUM-147

Table 1. Rare Earths Present in Fission Products

<u>Radionuclide</u>	<u>Half Life</u>	<u>% Fission Yield*</u>	<u>% Abundance**</u>
Y^{90}	64.2h	0.2	3.7
Y^{91}	59d	7.1	1.6
La^{140}	40.2h	7.5	<0.1
Ce^{141}	32.5d	6.9	<0.1
Pr^{143}	13.7d	6.6	<0.1
Ce^{144}	285d	3.9	29
Pr^{144}	17.3m	3.9	29
Nd^{147}	11.1d	3.2	<0.1
Pm^{147}	2.7y	0.7	10.7
Sm^{151}	90y	<0.1	0.1
Eu^{155}	1.7y	<0.1	0.14
Eu^{156}	15d	<0.1	<0.1

* In a reactor operating for 1 year at 1000 kw.

** One year after removal from a reactor which operated 1 year at 1000 kw.

Table 2. Recovery of Added Pm^{147} *

<u>Number</u>	<u>Percent Recovery</u>
1	61.2
2	70.7
3	82.4
4	83.7
5	53.8
6	72.0
7	72.0
8	75.8
9	61.2
10	66.6
11	65.6
12	72.5
13	86.5
14	70.1
15	82.4
16	61.5

Average Recovery = $71.1\% \pm 9.4\%$ at 66% CL.

* Recoveries included spiked water and spikes added to samples.

19-24844

LADC-6637

Secondary 997.6

cat

5-20-65

STATUS AND APPLICATION OF THERMOLUMINESCENT DOSIMETRY SYSTEMS*

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ABSTRACT

Thermoluminescence is broadly defined as the emission of light when a solid is heated to a temperature below that of incandescence. If the amount of light emitted can be related to the absorbed dose (or absorbed dose rate) deposited by ionizing radiation, the material can serve as the basis for a dosimetry system. Since the first report by Becquerel in 1883, a variety of thermoluminescent materials have been found. Recent developments have now made practical systems possible, the most highly developed ones utilizing appropriately "activated" LiF and CaF_2 . A few of the useful characteristics

*Work performed under the auspices of the U.S. Atomic Energy Commission.

of such systems include: a very great dynamic range, from a few mr to 10^4 r and higher; usually a very small loss of information before read-out, as low as 5% per year at room temperature; ability to measure extremely high radiation rates, 10^9 r/sec. in some cases; dosimeters can be made very small while retaining fairly good sensitivity, less than 1 r being measured by a 6-mm long by 1-mm diameter device. A wide range of applications has already been made in personnel dosimetry, tissue implantations, environmental studies, and in recoverable satellites. Although there may be a few limitations, thermoluminescent dosimetry systems will undoubtedly become increasingly useful and important dosimetric tools.

DISCUSSION

For many years work has been going on to devise various methods of measuring ionizing radiations of all kinds. One fruitful course of investigation has been in the field of "solid-state" detectors, photographic film and scintillators being perhaps the most notable examples. A variety of phenomena have been used, including: temporary or permanent changes in coloration, electrical conductivity, or light

transmission; light excited by light of shorter or longer wave-length; and thermally excited luminescence. Systems based on this last phenomena will be briefly described.

Thermoluminescence is defined in a general way as the emission of light when a solid is heated to a temperature below that of incandescence. If the amount of light emitted can be related to the energy or dose deposited, the material can serve as the basis for a dosimetry system. Since the first report by Becquerel⁽¹⁾ in 1883, a variety of thermoluminescent materials has been found, among them are CaF_2 , LiF , CaSO_4 , CaCO_3 , SiO_2 , SrSO_4 , and many others.⁽²⁾ Recent developments have now made some practical systems possible.

A thermoluminescent (TL) material has appropriate impurities or activators which provide metastable electron states within the crystal lattice. When ionization takes place as the result of energy absorption from incident radiation, some of the free electrons can become trapped in these states. If the material is now heated to a sufficiently high temperature, trapped electrons are released to return to the ground state with the possible emission of light in the visible and near-visible spectrum. Figure 1 is a schematic representation of this process.

There may be several energy levels of the traps, each requiring a different temperature for a given probability of electron release. Mathematically, the probability of electron escape as a function of the energy barrier, or "trap depth", and of the temperature of the material can be written as follows:⁽³⁾

$$p = s \exp (-E/KT),$$

where p = probability of escape per second,

s = proportionality constant of the order of $10^{8 \pm 1} \text{ sec}^{-1}$,

E = energy barrier or trap depth,

T = absolute temperature,

K = Boltzman's constant.

It can easily be seen that for a given temperature the probability of escape increases as the trap depth decreases.

The most useful materials are those whose traps are of such values that the probability of escape at ordinary room temperatures is extremely small (10^{-8} to 10^{-9} sec^{-1}) but approaches the value of 1 before reaching temperatures of incandescence.

The light emitted can be measured using the arrangement shown schematically in Fig. 2. The light intensity plotted

as a function of temperature, or as a function of time as the temperature is being increased, is called a glow curve. Such a curve for a hypothetical thermoluminescent material is shown in Fig. 3. The two peaks indicate the presence of two metastable traps. As the temperature of the material rises the probability of emptying traps increases with a resultant increase in light intensity. The intensity will begin to decrease when the number of unemptied traps becomes sufficiently small. Eventually the intensity will drop to zero as all the traps are emptied, unless there is another higher energy trap that becomes apparent or incandescence is approached.

In general, the total amount of light emitted during the heating process is proportional to the number of electrons released from the traps, excluding some very high temperature effects. The number of electrons placed into traps is proportional to the energy deposited in the material by incident radiation. Hence, the total light out is proportional to the dose received, provided the traps are at high enough energies. The trap indicated by the lower peak in Fig. 3 would loose significant numbers of electrons in a fairly

short time at ordinary room temperature. The peak height can also be used as a measure of absorbed dose. In this case, heating of the material must be done in a reproducible manner, because rate of heating affects the height obtained for a given dose, faster heating rates resulting in peaks of greater amplitude with the maxima shifted to higher temperatures.⁽⁴⁾

All the traps of the thermoluminescent material can be emptied by heating at a high enough temperature for a sufficiently long time. After cooling the material, it is now ready to measure another exposure to radiation.

The relative response versus exposure which is typical of several thermoluminescent materials is shown in Fig. 4. The curve indicates very good sensitivity; some dosimeters can measure considerably less than 1 milliroentgen total exposure. A dynamic range of the order of eight decades is a striking feature of many thermoluminescent dosimeters (TLD). Figure 5 shows the relative response versus energy for three of the more commonly used materials.⁽⁴⁾ The response of $\text{CaF}_2:\text{Mn}$ and of CaSO_4 are reminiscent of the energy dependence of film; both respond much like bone. The characteristics of

LiF are reasonably close to those of soft tissue and make it a particularly interesting material for use in dosimetry.

There are several commercial TLD systems now available. However, only the Edgerton, Germeshausen & Grier, Inc. (EG&G) Model 2 Thermoluminescent Dosimeter System and the Controls for Radiation (Con-Rad) TLD System will be described briefly, these being representative of the inherent capabilities of TLD systems in general.

The EG&G Model 2 Dosimeter, shown in Fig. 6, consists of $\text{CaF}_2\text{:Mn}$ coated on a coiled-wire heating element and encapsulated in an evacuated glass envelope.^(5,6) Two gold plated Kovar feed-throughs provide connection to a heating current supply. Because of the over-response of $\text{CaF}_2\text{:Mn}$ to low energies, indicated in Fig. 5, the detector is placed in a case consisting of an aluminum outer shell and a tin-lead energy compensation shield. Figure 7 shows a partially assembled detector and shield assembly and Fig. 8 indicates the energy response of the complete unit.

The Model 2 Reader is shown in Fig. 9. In the lower right hand corner the manner in which the detector is placed in a socket in the reading-head plug can be seen. The plug

is placed in the reading head with electrical connection being made between a set of spades on the plug and a set of contacts in the reading head. The read cycle is initiated by pushing the read button, after which current is passed through the heating coil, the light emitted by the thermoluminescent material is measured by a photomultiplier tube, and the resulting glow curve is drawn on the strip-chart recorder paper. The entire cycle takes approximately 20 seconds.

The peak of the curve is read directly on the scale printed on the paper. Automatic ranging is provided so that full scale can be any decade from 50 mR through 5000 R, depending on how much light is being measured during the read cycle. The resultant full scale is shown at the end of the cycle in the window where the word "empty" appears in Fig. 9. In addition, a pip appears on the right hand side of the chart each time a range change has been made. Some typical traces are shown in Fig. 10. As pointed out earlier, in order to be able to use the peak as the measure of the dose rather than the area under the curve, the material must be heated in a reproducible manner. When this is done it also means that the peak will occur at the same time after

beginning the heating. Thus, the peak of interest will always appear between the closely set lines near the scale figures shown in Fig. 9.

The main specifications of this CaF_2 system, as provided by EG&G,⁽⁶⁾ are listed in Table I.

TABLE I

1. Gamma Dose Range - 5 mR to 5000 R (present limits of reader).
2. Rate Dependence - none to at least 10^9 R/sec.
3. Energy Dependence - $\pm 10\%$ from 60 keV to at least 1.3 MeV (see Fig. 8).
4. Neutron Sensitivity in R/n/cm^2 :
 - a. Thermal - 1.41×10^{-10}
 - b. 5.4 MeV - 0.11×10^{-9}
 - c. 14 MeV - 1.47×10^{-9}
5. Reusability - in excess of 100 readings.
6. Stability - the device may be read-out at any time after exposure with negligible loss of information (less than 5% loss per year when stored in the case and the temperature does not exceed ambient).

7. Percentage Standard Deviation:

a. 100 readings of one dosimeter

1) $5 \text{ mR} - S_x = \pm 4\%$

2) $40 \text{ mR} - S_x = \pm 2\%$

3) $400 \text{ mR} - S_x = \pm 1\%$

b. 10 readings of 10 dosimeters

1) $5 \text{ mR} - S_{\bar{x}} = \pm 4\%$

2) $40 \text{ mR} - S_{\bar{x}} = \pm 2\%$

3) $400 \text{ mR} - S_{\bar{x}} = \pm 1\%$

8. Variance Among Dosimeters - $\pm 10\%$ of average at 90% confidence limit.

9. Accuracy - will depend on the details of calibration by the user. System has been checked at EG&G against a Co^{60} source calibrated by an NBS secondary standard. This results in multiple dosimeter readings within $\pm 15\%$ of reading or 2 mR, whichever is greater.

There is also available from EG&G a microdosimeter which is a sealed glass tube 1 mm in diameter and 6-mm long containing either $\text{CaF}_2:\text{Mn}$ or LiF powder. With a small adapting coil these can be read on the Model 2 Reader. The range covered is from less than 1 R to 10^5 R or greater. Two of

these microdosimeters can be seen on the black patch in the lower left side of Fig. 9.

The Con-Rad TLD system utilizes loose LiF powder,⁽⁷⁾ as shown in Fig. 11. The powder dispenser at the left side of the picture gives a standard charge of 58 mg. The plastic capsules used for individual dosimeters are approximately 5 mm in diameter and 20-mm long. To read the exposure, the powder is placed in a planchet which is then inserted in the reader. A controlled amount of electrical current is then passed through the planchet for a period of about 10 seconds. A photomultiplier tube measures the light emitted and a number proportional to the total light out is read on a digital voltmeter. The entire cycle is approximately 15 seconds long. Manual scale-ranging of two additional decades is provided, but it must be done only after completion of the cycle. Further changes in sensitivity are made by changing the voltage on the photomultiplier tube. Thus, some knowledge of the exposure is desirable.

An interesting feature of a LiF system is that its response to thermal neutrons can be changed considerably by varying the isotopic content of the Li component.⁽⁸⁾ Natural

Li has about 7.5% of Li^6 with a very high cross section for an (n,α) reaction. High-energy ionizing particles are thus generated which can deposit energy in the TLD material. Con-Rad type N and Harshaw TLD-100 contain the natural isotopic ratio. Con-Rad Type 7 and Harshaw TLD-700 are made from 99.993% Li^7 and have negligible thermal-neutron responses compared with the others.⁽⁴⁾ Harshaw TLD-600 is available and is highly enriched in Li^6 . In addition, if a thermoluminescent material is mixed with a hydrogen-rich material, alcohol for example, there may be an enhanced fast-neutron response.

The main specifications of this LiF system, as provided by Con-Rad,⁽⁹⁾ are listed in Table II.

TABLE II

1. Range - 10 mR to 10^5 R (lower limit 100 mR if N_2 flow during reading not used).
2. Rate Dependence - less than 5% to 3×10^{11} R/hr.
3. Energy Dependence - $\pm 5\%$ 10 keV to 1.3 MeV shielded.
 $\pm 40\%$ at 40 keV unshielded.
 $\pm 10\%$ at 100 keV to 1.3 MeV unshielded.

4. Neutron Sensitivity - [for Harshaw TLD-100 and TLD-700 only].⁽⁴⁾
 - a. Thermal
 - 1) TLD-100 2.7×10^7 n/cm² equals 1 R gamma-ray exposure.
 - 2) TLD-700 - less than 0.5% of response of TLD-100.
 - b. Fast - TLD-100 & TLD-700, 10^8 n/cm² less than 1 R gamma-ray exposure.
 5. Reusability - indefinite for accumulated exposures less than 10^5 R.⁽⁴⁾
 6. Stability - less than 5% per year at 20°C.
 7. Percentage Standard Deviation
 - a. 10 mR - $\pm 20\%$
 - b. 100 mR - $\pm 5\%$
 - c. 1 R - $\pm 2\%$
 8. Variation of weight of TL material dispensed - approximately 1%.
 9. Accuracy - will depend on the details of calibration of user. Typical value would be $\pm 5\%$ of precision number below 1R.
-

Two devices besides standard capsules are available from Con-Rad. One is the Ultra-MicroDosimeter, a 1.5-mm diameter by 10-mm long sealed glass tube containing LiF with

a usable range of 0.1 R to 10^5 R. The other device is the Health Physics-TLD Dosimeter, which is essentially a Con-Rad planchet with LiF powder held in the cup by a permanently attached fine-mesh screen. Its usable range is 0.01 R to 10^5 R. Both dosimeters are reusable.

Some drawbacks exist in the use of thermoluminescent materials and various precautions have to be taken if proper measurements are to be made. For example, when $\text{CaF}_2:\text{Mn}$ is used in air, there is a spurious thermoluminescence equivalent to about 1 R of Co^{60} gamma-radiation, which prevents the measuring of small doses.⁽¹⁰⁾ Enclosing the material in a vacuum or inert gas eliminates the difficulty, but often the wall of the containing vessel disturbs measurements of particle radiation such as electrons and beta-rays. Also, $\text{CaF}_2:\text{Mn}$ is sensitive to ultraviolet light⁽⁶⁾ and should not be exposed to room light for more than 5 or 10 minutes between dedosing by heating and the reading of a subsequent exposure. In the case of LiF when used in loose powder form, a spurious thermoluminescence equivalent to about 1 R of Co^{60} occurs when the powder is read while in an air atmosphere.⁽⁸⁾ It has been found⁽⁹⁾ that nitrogen gas is a specific quencher

of this spurious effect in LiF, so that if the reader enclosure is filled with dry N₂, an exposure as low as 10 mR can be measured. LiF undergoes permanent crystal damage for total accumulated doses greater than about 3×10^4 R, the degree of which depends on the total dose and on the number of exposure and read cycles which have taken place to obtain that total dose.⁽¹¹⁾ Thus, in some instances a record would have to be kept of all exposures of all the powder which is to be reused.

Thermoluminescent dosimeters have already been widely used. The physical characteristics and the cost of such systems compare favorably with film systems of personnel dosimetry. It is reasonable to assume that with further development, considerably better overall dosimetry systems will emerge than is possible with film. Some of the applications other than personnel dosimetry are: environmental studies, including background levels; implantation under the skin of animals left in their natural environment;⁽⁶⁾ and attaching to large insects; deep animal implantation⁽¹²⁾ to measure doses from either external radiation or internal radiation emitters; clinical and radiobiological dosimetry;^(8,13)

and space dosimetry by means of recoverable satellites.⁽¹⁴⁾

Many characteristics of thermoluminescent materials have yet to be subjected to detailed scrutiny, but their usefulness has already been shown. With further improvements and perhaps new materials, thermoluminescent systems will undoubtedly become increasingly important dosimetric tools.

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Fig. 1 - Schematic representation of the thermoluminescent process.

Fig. 2 - Schematic diagram of a thermoluminescent-dosimeter reader.

Fig. 3 - Glow curve of hypothetical thermoluminescent material.

Fig. 4 - Response vs. exposure typical of several thermoluminescent materials.

Fig. 5 - Dependence of thermoluminescence response per roentgen upon γ -ray quantum energy [after Attix (4)]. All data are normalized to 1.00 at 1.25 MeV (Co^{60} γ -rays). Curves are calculated on the basis of $(\tau + \mu_{\text{en}})/(\mu_{\text{en}})_{\text{air}}$, in cm^2/g , under the assumption of constant response per rad in the phosphor. Circled points were measured with miniature $\text{CaF}_2:\text{Mn}$ dosimeters irradiated by heavily filtered x-rays. Crosses represent the data of Cameron et al. (8), comparing bare LiF (TLD-100) powder with an NBS-calibrated Victoreen 25-R chamber.

Fig. 6 - EG&G thermoluminescent detector.

Fig. 7 - EG&G thermoluminescent detector and energy compensation shield.

Fig. 8 - EG&G thermoluminescent dosimeter relative energy response in shield.

Fig. 9 - EG&G Thermoluminescent Dosimeter Reader, Model 2.

A. 2.3 R -- TWO SCALE CHANGES
(Pipe on record in upper margin)

B. 33 MR -- BLACK BODY RADIATION
AFTER PEAK

C. ZERO -- BLACK BODY RADIATION
AFTER DOUBLE LINE

Fig. 10 - EG&G typical chart records.

Fig. 11 - Con-Rad TLD System.

PRELIMINARY RESULTS ON THE URANIUM CONTENT IN THE HUMAN DIET

George A. Welford
Ruth Baird

It is known that traces of uranium (0.76 microgram per gram)¹ are found in the earth's crust to a depth of 2900 kilometers. Natural waters² contain from 0.2 to 600 micrograms per liter. Human bone³, tissue, and organs have been analyzed and found to contain traces of uranium, usually less than 0.02 microgram per gram of organ. Several authors^{4,5} have reported measurable quantities of uranium in urine excreted by humans with no history of industrial exposure. These results vary but are usually less than one microgram per liter of urine. Hoffman³ reports the uranium content of various foods that range from 0.007 to 6.71 micrograms of uranium per gram of ash.

The tri-city diet study at HASL, for documentation of strontium-90 levels, presents a unique opportunity to systematically study the uranium levels in the human diet as monthly samples are taken at New York City, Chicago, and San Francisco.

Analytical Procedure

Approximately one gram of the dry ashed food material is weighed and transferred to a 250-ml beaker for uranium analysis. A known aliquot of uranium-232 (~1000 dpm), as tracer, is added to each sample and the organic material is completely destroyed by multiple evaporations with nitric acid and hydrogen peroxide. The salts are dissolved in 7N hydrochloric acid and passed through a conventional ion

exchange column of pretreated Dowex 1 X4 (100-200 mesh). The column is washed with 9N hydrochloric acid and the uranium, along with iron, is eluted with 1N hydrochloric acid. The elutriant is evaporated to dryness and the residue dissolved in 0.3N sulfuric acid. Iron is removed from this solution by mercury cathode electrolysis. The resulting solution is evaporated to dryness, dissolved with nitric acid and transferred to a 5-ml volumetric flask.

Triplicate 0.1 milliliter aliquots of the solution are dried and flamed on a platinum dish and fused with 100 milligrams of sodium fluoride. The fluorescence is measured by a HASL fluorimeter. An additional 0.1 milliliter aliquot, from the 5-ml volumetric flask, is pipetted onto a platinum dish, dried, an alpha phosphor added, and counted for tracer recovery.

This method is capable of the determination of 0.005 microgram of uranium per sample. A sodium fluoride fusion without added uranium ranges from 5-7 instrument deflections. A deflection unit is equivalent to 0.0001 microgram of uranium on the dish or one microgram per liter of solution. Accurate analysis for uranium at the submicrogram level must be concerned with the uranium content of the reagents used. Each analysis for the uranium content of a food was preceded and followed by a blank determination using the same quantity of reagents outlined in the procedure. This blank varied slightly but averaged 0.007 microgram which was about the same level of uranium we found in reagent grade calcium phosphate.

The overall recovery indicated by the tracer technique varied in different food matrices but generally was above 80%.

Several other approaches to the isolation of uranium from a food and bone matrix were attempted in the laboratory. Korkisch^{6,7} has recently published several ion exchange techniques that separate uranium and iron using a mixed solvent system. These are: diethyl ether and 0.03N nitric acid and either acetic, propionic, or butyric acid and 5N nitric acid. We achieved excellent separations using these mixed solvents and better than 90% recovery of the added uranium. When this procedure was applied to actual samples a basic acetate precipitate of iron was formed that carried a large percentage of the uranium. Some promising results were obtained using a paper chromatographic technique for uranium isolation and additional work is proceeding in this area.

Tables 1 through 4 compare some results for food material analyzed in our laboratory with the levels reported in the literature. A direct comparison is not feasible as no reference to the section of the country sampled was available. This preliminary work should yield a better understanding of the geographic distribution of uranium and its concentration in various food material.

Table 1

BAKERY PRODUCTS

<u>New York City</u>	<u>Chicago</u>	<u>San Francisco</u>
F0801	F0700	F0751
0.077 $\pm$ 0.012	0.066 $\pm$ 0.006	0.070 $\pm$ 0.009

Vienna Whole Wheat Bread (Hoffman)

1.24

Micrograms of Uranium/gram of ash

Table 2

WHOLE GRAIN PRODUCTS

<u>New York City</u>	<u>Chicago</u>	<u>San Francisco</u>
F0802	F0701	F0752
0.057 $\pm$ 0.009	0.056 $\pm$ 0.018	0.059 $\pm$ 0.008

Micrograms of Uranium/gram of ash

Table 3

FRESH VEGETABLES

<u>New York City</u>	<u>Chicago</u>	<u>San Francisco</u>
F0791	F0690	F0741
0.080 ± 0.009	0.076 ± 0.001	0.136 ± 0.010
Corn (Hoffman)		
0.007		
White Cabbage		
6.71		
Micrograms of Uranium/gram of ash		

Table 4

MISCELLANEOUS FOOD MATERIAL (HOFFMAN)

<u>Food</u>	<u>Micrograms of Uranium</u> <u>gram of ash</u>	<u>Micrograms of Uranium</u> <u>gram of material</u>
Corn Seed	0.007	
Animal Muscle	0.009	
Beef Blood	0.015	
Beans		8×10^{-5}
Yeast		2×10^{-3}
Chicken Egg		8.8×10^{-4}
Beef Liver		8.0×10^{-2}

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MEASUREMENT OF RADIUM-226 AND RADON-222 IN ENVIRONMENTAL SAMPLES

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For some time there has been increasing interest in the determination of the natural activity content of environmental samples, such as human bone and selected samples from the typical diet. One nuclide of particular interest is radium-226. Lately we have been trying to accurately document the Ra^{226} levels present in the environment.

Radium-226 is most easily determined by the classical technique of emanating and counting its gaseous daughter radon-222. This technique remains a unique and highly specific analysis in the determination of Ra^{226} . If any sample matrix can be reduced to a clear solution a radium separation is not necessary since emanation of Rn^{222} is so highly specific. However, for other reasons it is sometimes desirable or even necessary to perform a chemical radium separation. For example, most samples must be in an excessively large volume before complete solution can be effected. Sometimes a separation is necessary because the sample must be dissolved in a non-volatile solvent during emanation. Also, since radon exhibits a fair degree of surface activity, even small amounts of undissolved material have to be avoided.

Normally whenever a chemical separation is performed, it is helpful to have a gamma-emitting tracer present in order to estimate the radiochemical yield of each sample. For this purpose, Ba^{133} ($t_{1/2} \sim 7$ years) has proved to be adequate, since in the following methods the sample is in complete solution before the final RaBa precipitation. The radio-

chemical procedure should not introduce a significant amount of radium from reagents used in the separation and for this reason it is preferable to use distilled or organic reagents.

In the following procedures radium is separated from the bulk matrix by a simple RaBaSO_4 precipitation. The final $\text{Ra}^{226}\text{BaSO}_4$ precipitate is then dissolved in alkaline EDTA for emanation. The volume of this emanation solution is about 20 ml. After gamma counting for radiochemical yield the solution is placed in a radon emanation flask which has a total capacity of about 40 ml. A fritted glass base in the flask allows fine bubbles of the counting gas (85% N_2 + 15% H_2) to be swept through the solution, efficiently sweeping radon up into a stainless steel ion chamber which is used for counting radon. Counting gas is initially swept through the sample to establish time zero for the build-up of radon. The samples are then stored for at least a week (75% equilibrium) before the measurement is made. Duplicate emanations are performed on each sample to give an estimate of the error involved in the measurement.

Human Bone Ash

The procedure for determination of Ra^{226} in human bone ash is:

1. Weigh 10 grams of bone ash into a 90 ml glass centrifuge tube or 100 ml polypropylene centrifuge tube.
2. Spike the ash with an accurately weighed 0.1 g aliquot of Ba^{133} tracer solution (~4000 cpm/0.1 g).
3. Add 1 ml of Ba^{+2} carrier (20 mg/ml Ba^{+2}).
4. Add 20 ml of concentrated HCl (slowly at first to prevent foaming).

5. Stir and warm in an 85°C steam bath for about 5 minutes.
6. Add 10 ml of distilled H₂O.
7. Add 8-10 ml of concentrated NH₄OH (until a dense white permanent hydroxide flock forms).
8. Dissolve the flock in concentrated HCl (about 4 ml is required).
9. Add 2 ml of NH₄OAc (15 g/liter).
10. Add 1 ml of HOAc (20 ml glacial HOAc/liter).
11. Cool in a water bath to room temperature.
12. Add 1 ml (NH₄)₂SO₄ (100 g (NH₄)₂SO₄/liter).
13. Stir, remove stirring rod, and let the sample stand for one-half hour.
14. Add 1 drop of 0.1% Aerosol OT to reduce creeping of precipitate.
15. Balance pairs of centrifuge tubes with centrifuge cups.
16. Centrifuge at 2000 RPM for ½ hour. (3000 RPM if polypropylene tubes are used.)
17. Decant carefully and discard the supernate.
18. Add 5 ml of concentrated HCl and warm in an 85°C steam bath for 5 minutes. (Most of the BaSO₄ remains as a precipitate.)
19. Add 10 ml of distilled H₂O and add NH₄OH until a permanent flock forms.
20. Dissolve the flock in concentrated HCl and repeat steps 9-17.
21. Heat a solution of tetrasodium EDTA (300 g/l EDTA) and an EDTA wash solution (30 g/l EDTA) in an 85°C steam bath.
22. Break up the BaSO₄ precipitate with a stirring rod.
23. Add 1 ml of concentrated monoethanolamine, 5 ml of the hot EDTA solution and stir.

24. After 5 minutes, wash down the sides of the tube with about 10 ml of hot EDTA wash solution.
25. Let the tube remain in the steam bath for 15 minutes, stirring occasionally.
26. If some residual carbon particles are present, filter the hot, clear solution through a small #41 Whatman filter paper into a 1 oz polyethylene bottle.
27. Wash the tube and the filter paper with hot EDTA wash solution. Discard paper and residue.
28. Dilute the sample to the same liquid level as a known Ba^{133} spike solution (0.1 g of Ba^{133} spike solution diluted to 25 ml in a 1 oz polyethylene bottle). Cap and gamma count on a flat crystal to determine chemical yield.
29. Transfer to radon bubbler.
30. De-emanate radon by bubbling with forming gas for about 10 minutes at 200 ml per minute. (Record time as zero time for radon.)

With a four position centrifuge head, a total of 8 samples a day can be run by one person.

The average blank for the radium introduced by reagents in this procedure is 0.02 pc.

Table 1 shows the average radium recovery for samples of bone ash with added Ra^{226} corrected by the Ba^{133} yields:

Table 1

<u># Samples</u>	<u>Type</u>	Ra^{226} Recovery (%)	Ba^{133} Recovery (%)	Ra^{226} Recovery Corrected by Ba^{133} Recovery (%)
12	human bone ash	94.4±3.8	94.8±3.1	99.6±1.6

Vegetation or Vegetation Ash

The procedure for the determination of Ra^{226} in vegetation ash is:

1. Wash 10 grams of vegetation into a 400 ml beaker.
2. Spike the ash with an accurately weighed 0.1 g aliquot of Ba^{133} tracer solution (~ 4000 cpm/0.1 g).
3. Add 1 ml of Ba^{+2} carrier (20 mg/ml Ba^{+2}).
4. Add 100 ml of concentrated HNO_3 (slowly at first to prevent foaming).
5. Slowly evaporate to ~ 25 ml.
6. Add 100 ml of distilled H_2O .
7. Add concentrated NH_4OH (until a dense white permanent hydroxide flock forms).
8. Dissolve the flock in concentrated HNO_3 .
9. Add 2 ml of NH_4OAc (15 g/liter).
10. Add 1 ml of HOAc (20 ml glacial HOAc /liter).
11. Add 1 ml of $(\text{NH}_4)_2\text{SO}_4$ (75 mg SO_4 /ml).
12. Allow the sample to stand 1 hour at room temperature.
13. Filter the sample through Whatman #42. Discard the filtrate.
14. Place the filter paper in a platinum dish and ash at 500°C .
15. Remove the dish from the oven and cool.
16. Add 1 ml of concentrated H_2SO_4 and 10 ml of 48% HF .
17. Place the platinum dish on a sand bath and evaporate to H_2SO_4 fumes.
18. Cool the dish and transfer the contents with H_2O to a 90 ml centrifuge tube. (Carefully police the entire dish.)

19. Dilute the sample to ~80 ml.
20. Stir, remove stirring rod, and let the sample stand for one-half hour.
21. Add 1 drop of 0.1% Aerosol OT to reduce creeping of precipitate.
22. Balance pairs of centrifuge tubes with centrifuge dups.
23. Centrifuge at 2000 RPM for one-half hour. (3000 RPM if polypropylene tubes are used.)
24. Decant carefully and discard the supernate.
25. Heat a solution of tetrasodium EDTA (300 g/l EDTA) and an EDTA wash solution (30 g/l EDTA) in an 85°C steam bath.
26. Break up the BaSO_4 precipitate with a stirring rod.
27. Add 2 ml of 1:1 triethanolamine, 5 ml of the hot EDTA solution and stir.
28. After 5 minutes, wash down the sides of the tube with about 10 ml of hot EDTA wash solution.
29. Let the tube remain in the steam bath for 15 minutes, stirring occasionally.
30. If some residual carbon particles are present, filter the hot, clear solution through a small #41 Whatman filter paper into a 1 oz polyethylene bottle.
31. Wash the tube and the filter paper with hot EDTA wash solution. Discard paper and residue.
32. Dilute the sample to the same liquid level as a known Ba^{133} spike solution (0.1 g of Ba^{133} spike solution diluted to 25 ml in a 1 oz polyethylene bottle). Cap and gamma count on a flat crystal to determine chemical yield.
33. Transfer to radon bubbler.
34. De-emanate radon by bubbling with forming gas for about 10 minutes at 200 ml per minute. (Record time as zero time for radon.)

This procedure can be easily modified for raw vegetation samples by substituting a wet ashed vegetation sample containing carrier and Ba^{133} tracer for the vegetation ash and starting with step 5.

In the analysis of vegetation or vegetation ash samples, an Na_2CO_3 fusion should be avoided since this introduces a rather large and variable Ra^{226} background (~ 0.01 pc $\text{Ra}^{226}/\text{g Na}_2\text{CO}_3$).

The average reagent blank for radium introduced by radium in the reagents used in the vegetation procedure is 0.03 pc. Table 2 shows the radium recovery of vegetation ash samples with added Ra^{226} corrected by the Ba^{133} yields:

Table 2

# Samples	Type	Ra^{226}	Ba^{133}	Ra^{226}
		Recovery	Recovery	Recovery Corrected
		(%)	(%)	by Ba^{133} Recovery
9	hay ash and raw tobacco	85.6 ± 2.7	86.1 ± 2.7	99.5 ± 1.3

Radon Measurement

At HASL, 2-liter stainless steel ion chambers which count individual alpha pulses from radon and its daughters are used to measure Rn^{222} . All circuitry is transistorized and the number of counts recorded in each half hour interval is punched onto paper tape. The average background of 8 of these chambers ranges from 6-10 cph and 1 pc Rn^{222} yields 225 cph. These backgrounds are comparable to those of the small scintillation bell type chamber although the efficiencies are somewhat less.

However, their 2-liter volume allows radon to be swept from the sample with a relatively large volume of counting gas, thus insuring reproducible, 100% collection efficiency without an intermediate collection step. All samples are counted for at least 14 hours after allowing radon daughters to build up in the chamber initially for 5 hours. The formula for converting counting data to pc Ra²²⁶/sample, correcting for decay of radon during the counting interval is:

$$\frac{\text{pc Ra}^{226}}{\text{sample}} = \frac{(\lambda)}{(1-e^{-\lambda t})} \left| \frac{(\text{Total Cts in Ct Interval} - \text{Bkdg Cts in Ct Interval})}{(F) \left| \left(\text{Frac. Ba}^{133} \text{ Rec.} \right) \right| (225)} \right| - B$$

where

λ = Radon decay constant ($7.5532 \times 10^{-3} \text{ hrs}^{-1}$)

F = Build-up factor for radon in sample from $t = 0$

B = Reagent blank correction (pc)

t = Counting interval

225 = Calibration factor for HASL ion chamber (cph/pc)

Radon may also be determined in these chambers when the sample consists of a large gas volume such as an air sample. First, the radon must be collected in an intermediate step on activated charcoal so that the radon may then be transferred to the chambers with two liters of counting gas. The radon collection on charcoal we have found is easily accomplished with a trap (capacity ~50 g charcoal) which will withstand alternating dry ice temperatures and 500°C. The trap must also be vacuum tight, and have a gas inlet and exit valve. The collection system before

the charcoal trap includes two Fisher-Milliken gas washing bubblers, the first contains 100 ml monoethanolamine (for CO_2 removal) and the second 100 ml concentrated H_2SO_4 (for water removal). The bubblers are connected together with rubber tubing and also to the charcoal trap which should be packed in a bed of dry ice. At the exit of the charcoal trap it is convenient to have a wet test gas volume meter since this information is usually necessary. The system diagram is shown in Fig. 1.

Monoethanolamine is an efficient CO_2 scrubber and removes any CO_2 from the sample which would also adsorb onto the activated charcoal and, therefore, must be removed. Sulfuric acid is present in the system to remove water vapor which would not only freeze up in the trap reducing flow rates but which also displaces radon.

After the radon has been adsorbed onto the charcoal, it is quantitatively removed from the trap by heating the trap to 500°C for 10 minutes and then flushing the sample into an evacuated ionization

chamber with counting gas. With this system we have run 1000 liters of air containing a known radon concentration with 100% yield. Larger volume samples appear possible and this is under test in the laboratory. The radon blank in this system arises entirely from Ra^{226} present in the charcoal. The charcoal we have been using* contains 0.007 pc Ra^{226}/g . If the charcoal trap is first heated and flushed with counting gas to remove radon which has built up from radium, the radon background for a two hour sampling period is 0.005 pc.

* Barnebey-Cheney Activated Carbon Type HE2, Columbus 19, Ohio.

RECOVERY OF Am^{241} IN THE PRESENCE OF DTPA.

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Several laboratories have found that routine processing of urine specimens for determination of "gross alpha" activity is easier, more rapid, and has an equally good yield if alkaline phosphate precipitation direct from urine is used as the first step, rather than wet-ashing. It appeared desirable to determine whether this method would be equally effective in the presence of DTPA (diethylenetriaminepentaacetic acid).

We have investigated the recovery of Am^{241} in the presence of DTPA by the alkaline phosphate precipitation method. Results were compared with the wet ashing method, for spikes processed in aqueous solution, for human urine spiked in vitro, and for urine of rats injected with Am^{241} and DTPA. Recovery rates by the two methods were also compared when DTPA was not present. For the in vivo observations, 10 adult male Long-Evans rats were given doses of $0.1 \mu\text{C}$ Am^{241} in isotonic citrate containing 3 mg citrate per dose, injected intramuscularly in the left hind leg. Two hours later, half the rats received 50 mg of DTPA injected intraperitoneally. On the third day, the DTPA treatment was repeated and the control rats were sacrificed. Urines were collected at 24 hour intervals. The daily collection for each rat was diluted to 200 ml. This was divided into two equal parts, one of which was prepared by wet ashing and the other by alkaline phosphate precipitation at pH 8 with 6 M H_3PO_4 and 28% NH_4OH *. Subsequent processing consisted of BiPO_4 coprecipitation at pH 1.7 followed by coprecipitation as LaF_3 . The wet ash residues, the alkaline phosphate precipitates and the supernatants were all individually processed in this manner.

Results are shown in Figures 1, 2, and 3. From Fig. 1 it appears that in water or urine, recovery of Am^{241} from the alkaline phosphate precipitate is only slightly less than for the wet ash method. In the presence of DTPA, recovery in the precipitate is approximately 10%. Each bar in Fig. 2 represents the average of 5 rats. The rats showed wide individual variation in rate of excretion of Am^{241} with and without DTPA. Recovery of Am^{241} in the alkaline phosphate precipitates of rats which had not received DTPA was as good or slightly better than by the wet ashing method. The supernatants contained only traces of activity. In the rats which had received DTPA, recovery in the precipitate ranged from 39% on the first day to 7.7% on the sixth day, showing a constantly increasing supernatant-precipitate ratio (see Fig. 3), which probably reflects an increasing chelate/metal ratio in the urine excreted.

We have concluded from these results that at pH 8 Am^{241} is strongly chelated, and accordingly the alkaline phosphate precipitation method is not suitable for the quantitation of urinary alpha activity in patients who have been treated with DTPA.

* Because of the high dilution of the rat urines, it was necessary to add 10 mg Mg^{++} or Ca^{++} as carrier.

Figure 1 Comparative recovery of Am^{241} spiked in vitro by wet ashing and alkali precipitation.

Figure 2 Comparative recovery of Am^{241} from urine of rats treated with DTPA and from untreated rats by wet ashing and alkaline phosphate precipitation.

Figure 3

Increased chelation of Am^{241} with time.

THE USE OF COULOMETRY IN ROUTINE ANALYSIS

By

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The coulometric method has been applied to several problems encountered in industrial hygiene analysis. This report details some of the applications made and progress made in developing new procedures. The method has been applied to two general types of problems. The first is comprised of standard solutions and solutions where the interferences are low. The second comprises air samples collected for exposure evaluation.

General discussions of coulometry, both theoretical and applied, have been written by DeFord (1), Cooke (2), and Reilley (3). Only a brief outline will be discussed here. In coulometry a current is passed through the solution causing a desired electrochemical process to occur. In some cases it is necessary to control the potential of the generating electrodes so that only one reaction occurs. This is referred to as controlled potential coulometry. In others the current is controlled and the total number of coulombs consumed can be found by timing this constant current. This has been called constant current coulometry and, in our work, coulometric titration. It is essential that all of the current be used in the desired reaction. This is usually assured by design of the cell, electrode material, and concentration of the active species.

There are several advantages in using coulometric techniques over their conventional counterparts.

1. No standard solutions are required since the current serves this purpose. In addition, materials which are not stable may be used as titrants. Some examples are cuprous ion, free halogens, ferrous ion, and thallous ion. Solutions which are difficult to prepare and store, such as carbonate free base, may be generated with no difficulty. No dilution of the solution occurs when they are added.
2. The lower limit of detection is limited primarily by the current available and the sensitivity of the detection system. Generating currents of 0.2 milliamp have been successfully used. In one minute this is equal to 0.1 microequivalent.
3. The accuracy and precision are ordinarily extremely good. Under normal operating conditions we have obtained better than ninety-five per cent accuracy and precision of better than one per cent.

Instrumentation

The constant current source used in all our work was a Sargent Model IV. This provides regulated currents ranging from 4.8 to 98 milliamps. It has a running timer which provides for reading the results in terms of microequivalents. A constant source of current could also be conveniently obtained by using a battery and selected resistances.

The indicating and generating electrodes will be discussed with appropriate systems.

1. Determination of Acids and Bases

In a water solution containing an electrolyte, such as sodium sulfate, the passage of an electric current produces the following reactions:

The product of either of these electrode reactions can be used to titrate acids or bases if the electrodes are isolated. The generating electrodes used consisted of a platinum mesh and a coiled platinum wire. The end point may be determined as in the usual titration by using an indicator or pH electrodes. Care must be exercised in using an indicator since it might be destroyed at the electrode. We have used phenolphthalein in several instances but have found that combination glass-calomel electrode works quite well. Some typical results of acid standardizations are:

<u>Aliquot Titrated</u>	<u>Acid</u>	<u>Concentration</u>	<u>Result</u>
0.05 ml	HCl	6M	6.045 $\pm$ 0.009
0.250 ml	HCl	1M (volumetric standard)	1.0040 $\pm$ 0.001
0.05 ml	H ₂ SO ₄	3.3M	3.348 $\pm$ 0.009

Similar precision was obtained when sodium hydroxide was standardized by reversing the leads. The combination glass-calomel electrode was used in determining bases. The method has been used to determine acids and bases in air samples with no difficulty.

2. Use of Halogens as Titrant

Bromine and iodine can be quantitatively generated by oxidation of the appropriate halide at the anode. It is an efficient process which has wide applicability. Iodine can be generated and

reacted with thiosulfate and arsenite with good results. The former system has been applied to the determination of ozone in air samples. The ozone is absorbed in neutral potassium iodine which contains a measured amount of sodium thiosulfate. The iodine which forms by interaction with ozone reacts with the thiosulfate, and the excess thiosulfate is determined by titration with electrically released iodine. The titration is conducted in neutral solution and interference from nitrite is small.

The indicating electrodes consist of two platinum foils. The same generating electrodes previously described are used. The cell is shown in figure one. The course of the titration can be followed by measuring the current with a milliammeter. At the end point there is a rapid increase in the current. Figure two shows a typical manual plot.

The iodine system can also be used for the determination of arsenic in air samples. In this case the titration is recorded during generation using a Sargent Model XXI polarograph. Figure three shows a recorded titration. At the 0.5 milligram level, which corresponds to the Threshold Limit Value, an average recovery of 99.9% was obtained using pure solutions. Synthetic air samples have yielded an average recovery of 93% + 0.6%. The difference between the two results is due to loss of arsenic in a preliminary separation step. Under the conditions used antimony does not interfere.

Bromine is easily generated and may be used for titration of arsenic, sulfides, and mercaptans. We have used this system for the determination of ammonia in air and it may be applied to determination of ammonia resulting from Kjeldahl digestions. In this way one can analyze a wide variety of organic nitrogen compounds in air. Chlorine can also be easily generated and utilized in similar fashion.

3. Complexometric Titrations

The complexometric titration is an accurate method for determining many metal ions. The amount of a metal that may be determined is limited by the usual volumetric considerations. In 1956 Reilley (4) reported on the use of electrically released EDTA in titrations of this type which extends the method considerably. A solution of mercury-EDTA complex is titrated in a cell shown in figure four. There is a small amount of free mercury which is initially reduced which yields a typical titration curve. After the inflection point the

mercury in the chelate is reduced yielding free chelate. A measured amount of metal ion is added and the titration is repeated. The amount of metal present is determined by measuring the difference between the two curves. We have determined cadmium using DTPA as the complexing agent. Results in the 0.5 to 5.0 milligram range deviated from known values by less than one per cent. At the 0.1 milligram level results deviated by less than three per cent. The generating electrodes were a mercury pool and an isolated platinum wire anode. The indicator electrodes consisted of a mercury drop and calomel electrode. In 1962 Monk and Steed (5) modified this basic system for use in determining the chemical yield in radiochemical determinations. The indicating system consisted of two polarized mercury electrodes which increased the sensitivity. Some typical determinations included yttrium, cerium, and neodymium in the range from about three to thirty micrograms. With one exception the error was less than 1.5%. This technique will be studied in conjunction with separation techniques for further applications in radiochemical yield determinations.

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CELL USED FOR HALOGEN TITRATIONS

Figure 1

MANUAL TITRATION OF THIOSULFATE USING IODINE

- A - Blank
- B - Air Sample

Figure 2

Figure 3

CELL USED FOR COMPLEXOMETRIC TITRATION

Figure 4

A SIMPLE ANALYTICAL METHOD FOR ISOLATING
LOW LEVEL ALPHA ACTIVITY OF AMERICIUM-241
FROM PLUTONIUM IN A ROUTINE URINALYSIS PROCEDURE

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ABSTRACT

A method is described for the analysis of Am^{241} in human urine. Plutonium is extracted by thenoyltrifluoroacetone in a routine urinalysis procedure. Americium is isolated from the residue of this procedure.

The method involves addition of sufficient sodium hydroxide to redissolve aluminum hydroxide while coprecipitating americium on lanthanum hydroxide. Trivalent americium is oxidized to the hexavalent americyl ion by silver catalyzed peroxy-disulfate. Addition of ammonium fluoride stabilizes the americyl ion while precipitating lanthanum and accompanying alpha-emitting impurities as fluorides. Following manganous nitrate reduction to the trivalent state, the purified americium is recovered from the supernatant by coprecipitation with radiopure cerium. The cerium fluoride is counted in a low background proportional alpha counter.

The method is effective for quantitative separation of americium from the lanthanides, other actinides, iron and aluminum. Sensitivity is sufficient to detect activities as low as 0.50 dpm.

INTRODUCTION

In a plant handling aged plutonium there exists a potential for exposure to Am^{241} as well as to plutonium. This fact points to the worth of a program for continuous evaluation of possible low level chronic exposures and unsuspected acute exposures to americium through quantitation of metabolized Am^{241} in urine. Data from such a program might be used for estimation of Am^{241} body burden¹, and as a guide for medical therapy.

A differential analytical procedure for Am^{241} in the presence of urinary plutonium has been reported². However, the chemistry of this procedure is such that it does not provide a convenient means for simultaneous evaluation of concurrent plutonium. Therefore, only known or suspected americium exposures could be conveniently investigated without additional burden to our laboratory staff and its facilities.

Since nearly 1000 Rocky Flats employees are involved in some phase of plutonium manufacturing or laboratory operations, the magnitude of the plutonium urinalysis program is understandably large. The sampling frequency is also enhanced by those persons with known or suspected acute exposures and/or plutonium contaminated wounds⁴.

The number of samples has discouraged use of procedures requiring evaporation and wet-ashing of routine 24-hr urine samples. Our present Pu procedure consists of bismuth phosphate coprecipitation from acid-digested urine at pH 1 to 1.5, wet-ashing of organics, lanthanum fluoride coprecipitation, TTA extraction from aluminum nitrate solution, and electrodeposition⁵.

Chemical separation of americium from the residue from routine TTA extraction of plutonium offered the most obvious point from which to develop an overall routine procedure. Such a procedure would neither require expansion of our urine sampling program nor appreciably increase the demand on space and equipment.

Use of 20mg of La^{+3} carrier in the plutonium procedure presented a serious obstacle to development of the desired procedure. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, although chemically pure, is incompletely radio-purified before use by a reprecipitation procedure⁶. Its use introduces radioactinium and alpha emitting daughters which are present in the $\text{Al}(\text{NO}_3)_3$ residue. This amount of lanthanum would also seriously reduce apparent recoveries by absorption of americium alphas.

The most current methods⁶ used for separation of americium from the lanthanides at the time of the initial investigation involved ion exchange systems. The most promising system: cation resin-concentrated hydrochloric acid was investigated. Resins with various percentages of cross-linkage and varying mesh sizes were used. Am^{241} and γ -emitting La^{140} tracers were used to follow the progress of solute band displacement on the columns. The process of fraction collection was tedious, time consuming, and non-quantitative. It was apparent that the requirements of this technique were too rigorous for routine operation by technicians.

Moore⁷ conducted an intensive study of oxidants for oxidation of americium III to the hexavalent state and reported the successful development of a simple analytical radiochemical method for

americium based on quantitative oxidation of tracer americium to the sexivalent state.

This report strongly suggested the possibility that an effective separation procedure for americium could be devised through utilization of this technique.

DISCUSSION

Principle of Method

The oxidation potential for the americium (III)-(VI) couple is -1.69 volts ($[H^+] = 1M$)⁸. From this value it is apparent that only the strongest of oxidants, such as argentic oxide, peroxydisulfate and ozone are capable of producing sexivalent americium.

Decomposition of peroxydisulfate in water follows the reactions.

Decomposition according to reaction (1) takes place in alkaline, neutral, and dilute acid solutions. Reactions (2) and (3), for which the net reaction is $H_2S_2O_8 + 2H_2O \longrightarrow H_2O_2 + 2H_2SO_4$, take place in strong acid solutions, i.e., $[H^+] > 0.3M$ ⁷. Since hydrogen peroxide reduces Am(VI) to Am(III), it is apparent that acidity must be held at a low value in order that quantitative oxidation of Am(III) to Am(VI) may take place.

Moore⁷ extensively investigated such important variables as pH, reaction catalyst, concentration of oxidant, temperature and duration of oxidation, and nature and concentration of reductant for Am(VI) to Am(III). He reported optimum conditions for these parameters and our experiments bear out his findings. These conditions are incorporated into the procedure outlined in this report.

The major problem confronting development of the routine Am procedure, i.e., purification of Am from lanthanide elements and other alpha emitters, is easily resolved since addition of ammonium fluoride to the system, following peroxydisulfate oxidation, stabilizes americyl ion in solution while precipitating lanthanide elements and impurities as fluorides. Additional precipitations of lanthanum fluoride carrier increase the degree of americium purification.

Reducing agents in general are obvious interferences in the procedure.

EXPERIMENTAL

Removal of Interferences

a. Aluminum

The aluminum nitrate residue from the routine Pu procedure contains approximately 0.27 equivalent wts. of Al^{+3} , 0.014 equivalents of nitric acid, and 4×10^{-4} equivalents of lanthanum. 30 ml of 12N NaOH is sufficient to neutralize the acid, precipitate lanthanum hydroxide, and solubilize aluminum as aluminate.

b. Bismuth

Any bismuth contamination present in the aluminum nitrate residue is carried forward to the Am oxidation system where it presents an insurmountable problem. At the requisite low acidity of the oxidation step Bi^{+3} hydrolyzes and tends to carry Am(III) from solution before its oxidation is effected. This difficulty was eradicated by complexation of Bi^{+3} as BiI_4^- before precipitation of LaF_3 from bismuth - containing HCL solution.

c. Calcium

For cases of known acute plutonium exposure the urine samples are processed apart from routine specimens to avoid possible cross-contamination. The plutonium isolation procedure⁹ used involves wet-ashing of the total urine, a lanthanum fluoride coprecipitation and TTA extraction of plutonium from aluminum nitrate solution.

The residue from this procedure usually contains gross amounts of calcium. Addition of alkali to solubilize aluminum and isolate lanthanum hydroxide also produces a voluminous precipitate composed of calcium hydroxide and calcium aluminate. This precipitate is always difficult, if not impossible, to dissolve in a limited volume of 0.1N HNO_3 .

A sequestering agent was used in initial attempts to eliminate calcium interference. Calculation of the conditional solubility products^{*10} for calcium and lanthanum hydroxides in the presence of EDTA indicated that hydroxide formation should be masked for Ca^{+2} while La^{+3} would precipitate at pH 7 to 8. This event was experimentally observed. However, coprecipitation of Am with $La(OH)_3$ was erratic.

The calcium problem was circumvented by dissolution of the mixed basic precipitate in 2N HNO_3 ; adjustment of pH to 1.5, followed by coprecipitation of americium with bismuth phosphate.

*The thermodynamic constant corrected for effects of the side reactions: metal complex formation, ligand protonation, and ionic strength.

Table 1

SPIKE AND CONTROL RECOVERIES*

Nuclide Added	No. of Samples	Added Activity (c/m/1.5 liters)	Count Time Minutes	Mean Alpha Activity Recovered		Mean Recovery (%)	
				Wet Ashing	BiPO ₄	Wet Ashing	BiPO ₄
Am	5	553 [±] 15	9	465 [±] 14		84.1 [±] 2.5	
Am	5	553 [±] 15	9		422 [±] 13		76.1 [±] 2.4
Am	10	4.28 [±] 0.51	60	3.61 [±] 0.47		84.3 [±] 11	
Am	10	4.28 [±] 0.51	60		3.2 [±] 0.44		74.8 [±] 10.3
Pu	3	888	30	11.54 [±] 1.2**		---	
Th	3	328	60		2.17		0.66
E.U.	2	1130	90	Bkgd		---	
E.U.	2	1130	90		Bkgd		---

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

**Pulse height analysis of this sample indicates that the activity consists of Am²⁴¹ impurity present in Pu stock solution.

RESULTS

The procedure outlined in this report was investigated using urine pooled from nonexposed personnel for spikes, control samples and blanks. Since 1500 ml is considered to be the extreme case for an average single-day void at Rocky Flats, mixed urine samples were divided into portions of this volume for experimentation.

Spike samples consisted of raw urine into which known levels of pure americium²⁴¹ tracer were added. Am²⁴¹/M separations (M = Th²³², Pu²³⁹, enriched uranium) were studied by addition of known alpha activity levels of these materials to raw urine. Blanks were carried through with every set of spikes and controls.

Experimental samples were processed by either the routine Pu procedure⁶ or the wet-ashing procedure⁹. The aluminum nitrate residues were then analyzed according to the appropriate Am analysis procedure.

Recoveries on the resultant sample planchets were determined by alpha counting. Decontamination was based on comparison of resultant counts (corrected for blank value) to the known level of added activity. Recoveries of the various nuclides are shown in Table 1.

PROCEDURE

Special Reagents

12 N Sodium Hydroxide - Dissolve 480 gm of sodium hydroxide (NaOH-AR, pellets) in 500 ml of distilled water. Cool and dilute to 1 liter.

Bismuth Nitrate Solution - Dissolve 231.2 gm of bismuth nitrate [Bi(NO₃)₃ · 5H₂O-AR] in 600 ml of concentrated nitric acid and dilute to one liter with distilled water.

Lanthanum Nitrate Solution -

- a. Dissolve 10 gms of lanthanum nitrate [La(NO₃)₃ · 6H₂O] in 200 ml of distilled water.
- b. Add 50 ml of ammonium hydroxide and stir.
- c. Divide the suspension equally among four 90 ml pyrex centrifuge tubes. Rinse the beaker into the tubes with distilled water. Centrifuge at 2000 rpm for five minutes and discard supernatant.
- d. Add concentrated HNO₃ to tube #1 to just dissolve the precipitate and transfer to tube #2. Rinse tube #1 with 2-3 ml of concentrated HNO₃ and transfer rinse to tube #2. Transfer to tube #3 etc. until all the precipitate is in solution in tube #4.
- e. Redistribute the solution from tube #4 equally among four clean pyrex tubes.
- f. Add 10 ml of concentrated NH₄OH to each tube and centrifuge for five minutes.
- g. Repeat steps d, e, and f.
- h. Repeat step d and transfer the solution to a 250 ml graduate. Rinse the centrifuge tubes into the graduate with distilled water.
- i. Bring total volume in the graduate to 160 ml with distilled water. Store the solution in a glass-stoppered bottle. This solution contains 20 mg La⁺³/ml.

0.2 M Ammonium Persulfate - Dissolve 11.4 gm of ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-AR}]$ in distilled water in a 250 ml volumetric flask. Make up to 250 ml with distilled water.

10% Silver Nitrate Solution - 10 gm of silver nitrate ($\text{AgNO}_3\text{-AR}$) dissolved in 90 ml of distilled water.

2 M Ammonium Fluoride -0.1 M Ammonium Persulfate - Dissolve 37.0 gm of ammonium fluoride ($\text{NH}_4\text{F-AR}$) and 11.4 gm of ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-AR}]$ in distilled water in a 250 ml beaker. Quantitatively transfer the solution to a 500 ml volumetric flask and make to volume with distilled water. Store the solution in a polyethylene bottle. Prepare fresh weekly.

Manganous Nitrate Solution - $\text{Mn}(\text{NO}_3)_2$ 51%-AR.

Cerium Nitrate Solution - Cerous nitrate $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ is freed from thorium and radium alpha emitting impurities by a tributyl phosphate extraction procedure¹¹. The cerous nitrate stock solution obtained is used to prepare working solutions containing 4 mg Ce^{+3} /ml. The alpha activity of the carrier solution is reduced to at least 0.6 ± 0.3 alpha counts/hr/mg of cerium.

Special Equipment

Cone-Driven Stirring Motor - This device, equipped with an eight inch polyethylene stirring paddle, is used to provide rapid mechanical stirring of mixtures in 90 ml centrifuge tubes.

"Vortex Stirrer" - An excellent swirling effect is provided for many of the mixing, dissolution and washing steps called for in the procedures.

Sample Pretreatment

Transfer the aluminum nitrate residue to a 125 ml separatory funnel. Add 20 ml of toluene to the funnel and shake the mixture ten minutes. After phase separation, draw off the lower aqueous layer into a 90 ml pyrex centrifuge tube.

Mechanically stir the aluminum nitrate solution while adding 30 ml of 12N sodium hydroxide. Continue stirring until the aluminum hydroxide has redissolved and the solution has only a turbid appearance. Allow the precipitate to digest for five minutes. Centrifuge at 2000 rpm for five minutes; carefully decant and discard the supernatant. Proceed with the analysis as outlined under the appropriate sample type.

Coprecipitated Samples (Method A)

Wash down the walls of the 90 ml tube with distilled water from a wash bottle. Mix to break up the lanthanum hydroxide precipitate and transfer the suspension to a 50 ml graduated conical centrifuge tube. Repeat rinsing and transfer steps until the 50 ml tube contains 20 ml of suspension. Save the 90 ml tube. Centrifuge the 50 ml tube at 2000 rpm for five minutes. Aspirate and discard the supernatant.

Rinse down the walls of the 90 ml tube with 4N nitric acid from a wash bottle. Transfer the acid rinse to the precipitate in the 50 ml tube. Use a total of 10 ml of the acid. Swirl the tube to dissolve the precipitate. Stir the solution rapidly while reprecipitating lanthanum hydroxide with 10 ml of 12N sodium hydroxide. Allow five minutes for digestion. Centrifuge at 2000 rpm five minutes, aspirate and discard supernatant. Wash the precipitate with 20 ml of distilled water and repeat the centrifugation step. Proceed with the analysis as outlined under "Isolation of Americium".

Wet-Ashed Urines (Method B)

Dissolve the basic precipitate in a slight excess of 2N nitric acid. Transfer the solution to a 150 ml beaker. Rinse the 90 ml tube into the beaker with a small amount of distilled water. Adjust the pH of the solution in the beaker to 1.5 by dropwise addition of 12N NaOH. The final volume should be adjusted to approximately 65 ml.

Quantitatively transfer the solution from the beaker into a second 90 ml centrifuge tube and place the tube in a constant temperature oil bath at 80°C. Stir the solution mechanically while adding 1 ml of bismuth nitrate and 1 ml of concentrated phosphoric acid. Continue stirring at 80°C for one hour.

Remove tube from the oil bath and centrifuge at 2000 rpm for five minutes. Discard the supernatant solution and dissolve the bismuth phosphate in 20 ml of 4N hydrochloric acid. Add 0.5 ml of lanthanum nitrate carrier (20 mg La^{+3} /ml) and 0.5 gm of crystalline potassium iodide. Stir to dissolve potassium iodide and add 3 ml of concentrated HF. Allow the precipitate to digest five minutes, then centrifuge for five minutes at 2000 rpm. Aspirate and discard the supernatant.

Slurry 1 ml of 8N nitric acid with the precipitate. Stir and add a total of 30 ml of 2N nitric acid to dissolve the precipitate. Reprecipitate lanthanum fluoride by addition of 3 ml of concentrated HF. Centrifuge at 2000 rpm for five minutes and carefully aspirate the supernatant.

Add 5 ml of saturated boric acid and 5 ml of concentrated nitric acid to the tube. Stir to dissolve the precipitate and transfer the solution to a 50 ml graduated centrifuge cone. Rinse the 90 ml tube into the centrifuge cone with distilled water. Precipitate lanthanum hydroxide by addition of excess 12N sodium hydroxide. Centrifuge the tube at 2000 rpm for five minutes. Aspirate and discard the supernatant. Proceed with the analysis as outlined under "Isolation of Americium".

Isolation of Americium

Dissolve the lanthanum hydroxide precipitate in 2.5 ml of 1N nitric acid. Add 5 ml of 0.2M ammonium peroxydisulfate (prepared fresh daily) and 1 drop of silver nitrate (10%). Stir the mixture well and dilute to 20 ml with distilled water (pH should read approximately 1 with pHDrion paper).

Place the centrifuge tubes in a 600 ml beaker of hot water on a hot plate. Insert a thermometer into the tube containing the blank sample and note the time at which the temperature reaches 85°C. After 10 minutes oxidation at 85°C, add an additional 2 ml of 0.2M ammonium peroxydisulfate. Mix and continue heating for two minutes.

Remove centrifuge tubes from the hot water bath and immediately add 5 ml of 2M ammonium fluoride -0.1M ammonium peroxydisulfate solution. Stir well and transfer the tubes to a 600 ml beaker containing cool water. Allow 5 minutes for digestion. Centrifuge tubes at 2000 rpm for five minutes. Carefully decant the supernatant into a graduated 50 ml centrifuge tube. Wash the precipitate once with 2 ml of 2M ammonium fluoride -0.1M ammonium peroxydisulfate. Centrifuge three minutes at 2000 rpm. Add the wash solution to the oxidized supernatant.

Add 1 ml of manganous nitrate solution to the combined supernatants; mix and allow the tube to stand five minutes. Add 0.5 ml of cerium carrier. Mix, allow the precipitate to digest five minutes, then centrifuge for three minutes at 2000 rpm. Add 0.5 ml of cerium carrier to the supernatant. Mix with a platinum rod, being careful not to disturb the precipitate. Allow five minutes for digestion, then centrifuge at 2000 rpm for five minutes. Carefully aspirate supernatant and discard.

Wash the precipitate with 2 ml of 1M hydrofluoric -1M nitric acid. Centrifuge at 2000 rpm for five minutes. Aspirate and discard supernatant. Quickly invert the tube over a pad of absorbent tissue; allow to drain for fifteen minutes.

Slurry the cerium fluoride with a small amount of 1M nitric acid using a disposable capillary pipet. Quantitatively transfer the precipitate to a clean 2 inch stainless steel planchet. Dry the sample under an infra-red lamp. Flame the dried sample to red heat over a burner, cool and count in a low background proportional alpha counter.

SUMMARY

Method A described above is used currently at Rocky Flats for a routine radiochemical determination of americium²⁴¹ which coincides with our plutonium urinalysis program. The analysis of 1 blank, 2 spike controls, and 13 samples can be completed in fewer than five hours of operator time. The resultant sample is essentially free of other actinides and alpha emitters.

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THE DETERMINATION OF U^{235} BY PULSE HEIGHT ANALYSES

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Introduction

Uranium-235 in $>.01$ mg amounts may be detected by gamma scintillation counting on the .184 Mev peak of a pulse height analyzer. The technique requires that solid or liquid samples be placed in 4 ml vials and gamma counted in a NaI well-type crystal. These counts are compared to a U^{235} standard counted in the same manner. The following report describes the equipment and procedure used.

Preparation

Burnable solid samples are ashed and pulverized to a homogeneous powder. Other solid samples are prepared so they can be placed into a 4 ml vial. The 4 ml vial, which will contain the sample, is numbered and weighed. The vial is filled no more than half full in order to obtain a geometry similar to the Uranium standard. (The U^{235} standard used is a 2 ml solution which half fills the vial.) The vial is re-weighed to determine the sample weight and counted in the pulse height analyzer.

Liquid samples are analyzed by pipeting a 2 ml aliquot of the liquid directly into a 4 ml vial and counting the sample in the analyzer.

Counting

The equipment used for counting includes the following:

- Pulse Height Analyzer, Single Channel, Differential
- Linear Amplifier
- Pre-Amplifier
- Scaler and High Voltage
- Sodium Iodide (Thallium) Well-Type Crystal (1-3/4" x 2") with
- 2" Lead Shield

The sodium iodide well-type crystal system is enclosed in a 4' x 4' x 3' high, 4" thick, lead brick cave which is lined with copper. This shielding reduces the background for this system to approximately 5 c/m when counting on the .184 photo peak.

To calibrate the analyzer, a Cesium-137 standard is used. The base line is set at .662 Mev and the window width at 1. The gain is adjusted to obtain the maximum count on the .662 Mev peak of Cesium-137. The Cesium-137

source is then counted at the baseline, 30 Kev, with the window wide open as a check on Cesium-137 efficiency. (A 29% efficiency for Cesium-137 should be obtained.) Once this is done, Uranium is counted by setting the baseline on .184 Mev and the window width at 2. The 2 ml Uranium-235 standard is counted for five minutes and the count rate recorded. Prepared samples in the 4 ml vials are counted in the same manner. However, longer or shorter counting times may be used depending on the activity present in the samples. If low activity is present, the background of the well should be subtracted from the sample count.

Calculations

The formula used for calculating mg of Uranium-235 per sample is as follows:

$$\frac{\text{Sample c/m}}{\text{Standard c/m}} \times \text{mg U}^{235} \text{ in standard} = \text{mg U}^{235}/\text{sample}$$

If the Uranium-235 enrichment is known, the total uranium of a sample may be calculated as follows:

Example: A 2 ml acid waste solution containing 93.2% Enriched Uranium is counted along with a 15.76 mg U²³⁵ standard.

$$\frac{4323 \text{ c/m (Sample)}}{6100 \text{ c/m (Standard)}} \times \frac{15.76 \text{ mg}}{.932} = 12.0 \text{ mg Uranium/sample}$$

$$\frac{1.2 \times 10^4 \text{ ug}}{2 \text{ ml}} = 6.0 \times 10^3 \text{ ppm total Uranium}$$

Discussion

The .184 Mev peak is specifically proportional to the Uranium-235 content of Uranium samples. By counting at .150 to .200 Mev, the area under the .184 Mev photopeak will not detect other Uranium, Radium, or Thorium Gamma activities, thus eliminating their interference. Procedures by Morrison and Cosgrove have been used to determine Uranium-235 in which a multi-channel gamma spectrometer was used to scan the entire Uranium spectrum and measure the area under the photopeaks of samples compared to standards. Essentially the same results may be obtained more directly, and with less expensive equipment, by using scaler readings from a single channel pulse height analyzer.

There are a number of reasons why the pulse height analyses technique is more advantageous than wet chemistry in particular volumetric or fluorimetric procedures:

1. There is little or no sample preparation
2. Most samples do not have to be destroyed
3. Samples are counted directly
4. A large number of samples can be analyzed in a short period of time.

Comparative Results

FIGURE I

Duplication of Results by Different Operators

<u>Type Sample</u>	<u>Operator #1 Uranium-235 mg/gm</u>	<u>Operator #2 Uranium-235 mg/gm</u>	<u>% Difference</u>
Acid Leach Solution	0.483	0.480	1
Salt Bath	1.06	0.999	6
Residue from Leach	1.31	1.390	6
Vapor Blast Grit	2.07	2.10	1

FIGURE II

Wet Chemistry Versus Gamma Spectrum

<u>Type Sample</u>	<u>Wet Chemistry C. E. Inc. Uranium-235 mg/gm</u>	<u>Gamma Spectrum C. E. Inc. Uranium-235 mg/gm</u>	<u>New Brunswick Laboratory Uranium-235 mg/gm</u>
Acid Leach	0.483	0.482	
Acid Leach	0.490	0.490	
Salt Bath	0.90	0.98	
Vapor Blast Grit	0.77	1.17	1.30
Residue from Leach	1.52	1.35	1.25

THE SIMULTANEOUS DETERMINATION OF CALCIUM, STRONTIUM, AND BARIUM
IN BONE ASH BY RADIOCHROMATOGRAPHY

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Our laboratory has a moderate requirement for trace analyses of stable elements. We measure strontium in bone and milk by flame photometry. In this method the strontium is concentrated by a collection step which reduces the accuracy of our analysis.

To measure strontium by activation analysis, the cost is high when a number of samples are analyzed, and the installation of a neutron generator is not really justified.

Emission spectroscopy has offered the same problems as flame photometry.

We have been investigating a paper chromatographic method where only micrograms of a sample are used for direct analysis. The measurement of a bone sample for strontium has a sensitivity as low as attained by a neutron generator having a flux of 10^{12} neutrons per square centimeter. The detection limits for barium and calcium are much lower.

With our method, strontium, barium, and calcium are separated from each other and from microgram quantities of bone on a paper chromatogram by solvents already established in the literature. After separation, these elements are precipitated and tagged by a precipitant that is migrated along our chromatogram by a suitable solvent. This solvent moves the precipitant to the end of the chromatogram in order that the activity of the precipitant does not interfere with the analysis of our element.

Most of our work has been done with sulfuric acid tagged with S^{35} . We find that small quantities of strontium, barium, and calcium are quantitatively precipitated with dilute sulfuric acid.

To measure these elements we locate them on our chromatogram after they have been tagged, and count S^{35} activity. This activity is then related to microgram quantities of barium, strontium, and calcium by a curve which has been made from the S^{35} counting rate associated with various known amounts of these elements directly precipitated by chromatography.

The precipitation of calcium with radiofluorine has been attempted by J. V. Kudahl of the University of Birmingham. Here calcium and radiofluorine are mixed in a micropipette, applied to a chromatographic strip, and introduced to an ammonia atmosphere to raise the pH of the calcium solution and precipitate calcium fluoride. The strip is irrigated with a fluoride solution to remove excess radiofluorine.

Large amounts of calcium have been measured by precipitating calcium with C^{14} tagged oxalic acid and counting the calcium fluoride by liquid scintillation counting.

In our initial attempts to measure calcium, strontium, and barium we obtained a solution of sulfuric acid tagged with S^{35} . This solution when made up to 3/10 normal had a specific activity of 10^7 disintegrations per minute per gram of solution.

We spotted known quantities of strontium, barium, and calcium on one-half inch strips of Whatman No. 42 chromatographic paper in one microliter amounts, and the strips were developed for sixteen (16) hours in glass tanks with ethanol and water (1:1 quantities) by descending chromatography.

Solvents were investigated on the basis of whether (1) it would migrate sulfuric acid (the sulfate ion) along the chromatogram and (2) it would prevent the sulfate precipitate from becoming soluble.

To measure the amount of strontium, barium, and calcium, liquid scintillation counting was used. A $3\frac{1}{2}$ centimeter section of the strip, cut where our elements were precipitated, allowed the sample to be placed in a vial with fifteen (15) milliliters of liquid scintillator which was then assayed in a Packard tritium-carbon¹⁴ counter for the S³⁵ counting rate.

The counting rate of these sections was found to have a linear relationship with varying amounts of each element.

We analyzed each 3.5 centimeter length of these chromatograms to determine how the tagged sulfuric acid moved with this solution. Ninety-six to ninety-eight per cent of the S³⁵ activity was detected close to the solvent front. However, the small percentage remaining on the length of the strip gave us a background reading equivalent to our curve.

By washing the paper for three (3) days with 3 normal hydrochloric acid and ethanol and by adding methanol to our solvent, the background S³⁵ activity of the strip was decreased considerably.

Separation of Strontium, Barium, and Calcium in Bone

To determine the conditions for separating strontium, calcium, and barium in bone, quantities of strontium and barium carrier were added to a solution made of 100 milligrams of bone and 10 milliliters of 3N hydrochloric acid. Calcium is already present in the bone. Five, ten, and twenty-five microliters of this solution was applied to strips of Whatman No. 42 chromatographic paper. The strips were developed in a chromatographic tank

with 40% ethanol, 40% methanol, and 20% 2N hydrochloric acid as a solvent by descending chromatography.

To determine the movement and separation of strontium, barium, and calcium, the sample strip was sprayed with 8-OH quinoline, exposed to ammonia in a glass tank, and examined under ultraviolet light.

Also, the separation of these elements was studied by adding radioactive tracers of Ba^{133} , Sr^{85} , and Ca^{45} activities to the same concentrations of bone.

Separation here was determined by scanning for barium, strontium, and calcium with a chromatographic scanner. These sections of the strip were then cut out.

Calcium was determined on the strip by beta counting the Ca^{45} activity. The sections that were removed were counted on a large sodium iodide crystal to determine the amount and the separation of Ba^{133} and Sr^{85} .

A good separation of strontium, calcium, and barium in both investigations was indicated where 5 and 10 microliters of the bone (this is equivalent to 50 and 100 micrograms of bone) were used.

Determination of Strontium, Barium, and Calcium in Bone

In measuring strontium, barium, and calcium in a sample, the sample would be spotted on a pretreated Whatman No. 42 strip of paper 5 centimeters wide and 66 centimeters long, in the amount of 100 milligrams of bone where strontium and barium were to be measured and 10 micrograms of bone where calcium was to be measured.

Adjacent to these samples spots would be the same bone matrix with Ba^{133} and Sr^{89} added where strontium and barium were to be determined or Ca^{45}

added where calcium is to be determined.

This strip would be developed by chromatography with ethanol, methanol, and 2N hydrochloric acid as the solvent.

After the strip is removed from our solvent and air dried, tagged sulfuric acid is added above the sample origin and cold dilute sulfuric acid added above the bone matrix that we are using to locate strontium, barium, and calcium. This strip is then put into a solvent of methanol, ethanol, and water 25%/25%/50%. After sixteen (16) hours of developing the strip is removed, dried, and the location of strontium, barium, and calcium is determined by scanning the strip where our reference mixture has migrated.

We measure the amount of strontium, barium, and calcium in the sample by cutting out sections of the sample adjacent to the areas where Ba^{133} , Sr^{89} , and Ca^{45} have been located in our reference mixture. These strips which are 3.5 centimeters by 1.5 centimeters are counted with liquid scintillation counting.

The quantities of barium, strontium, and calcium in our sample is obtained from the counting rate of gas.

This chromatographic method also has potential uses in measuring most elements in trace quantities by using other precipitants such as Cr^{51} labeled chromate, Ti^{44} labeled titanate, Zr^{95} labeled fluorozirconate, C^{14} labeled carbonate, S^{35} labeled sulfide, and P^{32} labeled phosphomolybdate.

THE DIRECT MEASUREMENT OF RADIONUCLIDES IN BIOASSAY
SAMPLES BY MULTIDIMENSIONAL GAMMA-RAY SPECTROMETRY

by

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19:32

Introduction

The direct measurement of radionuclides in either whole or ashed bioassay samples has had limited application because of both the relatively large amounts of natural K^{40} which are present and their over-all low radioactivity levels. The normal presence of K^{40} with its characteristic high energy gamma radiation (1.47 Mev) drastically limits sensitivities for the direct gamma-ray spectrometric measurement of other trace radionuclides. Since the decay of most radionuclides involves the emission of two or more photons in cascade, the coincidence measurement of the characteristic photon energies of a given radionuclide provides a unique indication of its presence as well as a measure of its abundance.

In this present work a detector system was used which provided ultra-low background and high counting efficiency plus minimum Compton response and at the same time uses coincidence techniques to make use of the individual gamma-ray decay characteristic of each radionuclide for its identification and measurement. In this spectrometer system the sample is viewed by two large detectors for normal and coincidence gamma-ray spectrometry and the detectors are contained in a third detector which serves as an anticoincidence annulus for Compton and background suppression. A multiparameter analyzer is used for storing the normal and coincidence spectra.

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The observed concentrations of Hanford produced Na^{24} , Cu^{64} , As^{76} , Co^{60} , Sc^{46} and Zn^{65} in bioassay samples from Richland, Washington residents are reported and compared with the levels in their drinking water. The levels of cosmic ray produced Na^{22} and also of Cs^{134} in bioassay samples are compared with the observed levels in the principal foods of the diet. The advantages of this instrumental method over whole body counting and other bioassay methods are discussed.

Instrumental Method

The spectrometry system⁽¹⁾ used in the work reported here was a Nuclear Data 4096 channel analyzer used in a 64×64 channel grouping arrangement in conjunction with two anticoincidence shielded 4 inch thick by 6 inch diameter NaI(Tl) detectors (See Figure 1). One of the 4 inch by 6 inch detectors has a 4 inch light pipe of pure sodium iodide which serves to shield the detector from gamma radiation originating in its phototube. The anticoincidence annulus is a $11\text{-}1/2$ inch diameter by 12-inch long NaI(Tl) crystal with a $6\text{-}1/2$ inch diameter center hole to accommodate the principal detectors. The analyzer is supplied with an Optikon photographic printer which permits a readout of the entire memory in about four minutes. A Tally paper tape unit can be used as a readout for computer calculation. The sample to be measured is sandwiched between the two 6 inch diameter detectors. The signals from the two detectors are fed to the two separate analog to digital converters of the analyzer for energy analysis and from there to the memory storage unit. When a single photon interacts with one of the detectors, the event is stored on the corresponding X or the Y axis of the memory. When two photons are emitted simultaneously, each interacting with a separate detector, the event is stored in an energy-energy plane at a point uniquely characteristic of the two energies. The spectra of Cu^{64} and Co^{60} illustrate (Figures 2 and 3) the manner of storage. The normal spectra of these radionuclides as seen by

one of the detectors is shown for comparison. With a detection system of this type the unique decay characteristic of many radionuclides are readily resolvable thus permitting a far greater sensitivity for detection and direct measurement of many minor radioactive constituents.

In addition to the much greater selectivity provided by this multidimensional analysis, a much lower background (10^3 to 10^5 lower) is obtained.

Background and Backscatter Reductions

To illustrate the background reduction achieved in the detector system for single crystal response, measurements were made of the single 4 inch by 6 inch crystal alone and with sodium iodide and anticoincidence shielding. All of these background measurements were made inside a 4 inch thick lead shield and are shown in Figure 4. The top curve is the normal crystal background. The next curve down is the background obtained with the 4 inch long pure NaI light pipe between the crystal and its phototube and represents about a 20 - 50 per cent background reduction. The bottom two curves are background measurements of this crystal with its associated light pipe placed inside the annulus and with a second 6 inch diameter by 4 inch thick crystal above it as shown in Figure 4. It is evident that the background is reduced somewhat simply by the NaI shielding in this arrangement. When the output pulses from the annulus and top crystal are connected in anticoincidence with the principal detector a very substantial total reduction is obtained ranging from a factor of 5 to 10 except at the K^{40} peak.

To store a background count in the energy-energy plane, a gamma-ray interaction (or cosmic-ray shower, etc.) must occur in each of the two principal detectors simultaneously. The probability of such an event occurring can be greatly reduced by covering the area between the detectors which is not occupied by the sample

with a lead absorber. Such an arrangement provides an additional benefit in minimizing backscatter between these detectors as will be pointed out. In practice, 6-3/8 inch diameter lead absorbers of 1/2 or 1 inch thickness with centerholes the size of the samples (1 to 2 inches in diameter) are used. The effect on the background in the energy-energy plane of using lead absorbers, and the anticoincidence shielding (provided by the NaI(Tl) annulus) is shown in Figure 5. Figure 5 presents curves of the background counting rate on an energy diagonal extending from 0 to 3 Mev in the energy-energy plane. The top three curves show the backgrounds obtained with no absorber, and with a 1/2 inch and 1 inch thick lead absorber (with 1 inch diameter center holes) between the crystals. The crystal spacing was increased to 1/2 inch and to 1 inch respectively to accommodate these absorbers; however, it has been observed that increasing the crystal spacing from 0 to 1 inch only reduces the background by about 25 per cent. The background reductions relative to the no-absorber curve average about a factor of 2 and 4 respectively for the 1/2 inch and 1 inch absorbers. In the anticoincidence mode of operation these backgrounds are reduced by an additional factor of 5 to 20. If one selects a 1 inch thick absorber the total decrease in background over that obtained without the absorber and without anticoincidence ranges from a factor of 20 to 50.

In Figure 6 the background of the single 4 inch thick by 6 inch diameter crystal without lightpipe or anticoincidence is compared with that of the two detectors in the multidimensional detector system separated by 1 inch thick lead absorber-sample holder. The background shown for the multidimensional detector system is for an energy diagonal from 0 to 3 mev and therefore represents the case of 0 to 3 mev adsorption by each detector. One may wish to compare a point on the single crystal background with one at about half that energy on the multidimensional background if total absorption (of two gamma-rays) is considered in each case. However, by either method of comparison the background reduction with

multidimensional analyzer is three to five orders of magnitude lower than with the single crystal spectrometry.

In addition to suppressing the coincidence background the lead absorbers serve to reduce backscatter between the principal detectors. One of the problems of high geometry detector arrangements such as this is that some of the single gamma rays which interact with one of the detectors are backscattered and absorbed by the second crystal thus producing a coincidence pulse which is stored in the energy-energy plane. This effect is, of course, minimized by use of the lead absorbers. Figure 7 shows backscatter curves of Zn^{65} in the energy-energy plane on a constant energy line connecting the X and Y axes. These curves are for a point source with no absorber and with the 1/2 inch and 1 inch thick absorbers with 1 inch diameter center holes. The curves are normalized to a counting rate of 10,000 counts in the peak channels on the X and Y axes. It is evident that the absorbers reduce backscatter by factors of 8 to 50. This fact becomes especially important in the measurement of trace constituents in biological materials where large amounts of natural K^{40} are present. This radionuclide decays by emission of a single 1.47 Mev gamma ray and its contribution in the energy-energy plane due to backscatter is a problem. Figure 8 shows the backscatter curves for a point source of Co^{60} measured in a similar manner. The constant energy line in this case connects the two addition peaks at 2.5 Mev on the X and Y axes and shows the two coincidence photopeaks (used for Co^{60} measurement) in the energy-energy plane. The X and Y axes counting rates are again normalized to 10,000 counts and the curves show the large backscatter reduction effected by the lead absorbers.

Counting Efficiency

The sensitivity for the measurement of a given radionuclide is dependent on the instrument's counting efficiency as well as the background counting rate

and the Compton interference from other radionuclides.

In Figure 9 the efficiency for total absorption of a gamma-rays originating in the sample by either crystal is plotted as line 2E. The curve $2E^2$ gives the efficiency for two coincidence gamma rays to be totally absorbed - one each by the two detectors. This curve thus gives the probability that a coincidence event in the sample will be stored in a total absorption peak (either one of the two) in the energy-energy plane. It is plotted for the special case where the two gamma rays have equal energy but it does serve to illustrate the change in efficiency with energy.

It is evident that with this relatively high geometry system coincidence counting rates can be measured with a reasonably high efficiency. This fact coupled with the extremely low backgrounds and the elimination of most of the Compton interference makes the device an extremely sensitive and selective instrument.

For example, the Sc^{46} in a sample can be measured at an efficiency of about 12 per cent (or 6 per cent with the 1 inch lead absorber). The background with the absorber is about 1 count per hour. A sample containing 2 d.p.m., would therefore give 120 counts in 1,000 minutes above a background of about 15 counts.

Radionuclide Concentrations in Bioassay and Food Samples

Sample preparation for urine samples involved evaporation to dryness a few times with HNO_3 to destroy the organic material. The food samples are simply ashed overnight at $450^\circ C$. The ashed samples are then pressed into a standard 2 inch diameter by 1/2 inch thick metal ring. The exposed ends of the sample are covered with an adhesive tape to prevent loss during subsequent handling and counting.

The cooling of Hanford reactors by a one-pass circulation of Columbia River water through them induces a wide spectrum of trace radionuclides in the water. Subsequent use of Columbia River water at Richland, Washington and other cities for domestic purposes provides one route for radionuclide uptake by man. Although several radionuclides are present in river water they are not readily measurable in people by whole body counting. The radionuclides Zn^{65} and Na^{24} can often be detected by whole body counting.⁽³⁾ By multidimensional gamma-ray spectrometric analysis the radionuclides Cu^{64} , Na^{24} , As^{76} , Sc^{46} , Zn^{65} and Co^{60} have been observed in ashed urine samples from Richland, Washington residents. In addition the radionuclides Na^{22} , Cs^{134} as well as Cs^{137} are measurable in urine sample taken both locally and from other locations in the world. Such measurements permit one to estimate the whole body burden of these radionuclides.

Although many of these radionuclides and several others which are present in Columbia River water can be more easily measured in fecal samples, such results are of limited value since they include radionuclides which are passing through the body via the gastro-intestinal tract and have not been in the blood stream.

The group of radionuclides which can be measured in urine samples by direct counting are listed along with the coincidence gamma rays used in their measurement in Table I. In Table II some of the typical concentrations of these radionuclides in urine samples are listed and compared with observed values in drinking water from Richland. The radionuclide concentrations in the urine samples are extremely low and body burdens calculated from these excretion rates are inconsequential; however, the available sensitivity of the instrument does permit one to make measurements of uptake rates, excretion

rates and to estimate whole body burdens at these low levels. Although drinking water is probably responsible for man's main exposure to the short-lived radionuclides in Table II, it is well known that many of the longer-lived radionuclides are concentrated in various foods which could provide a much more significant source. Crops which are irrigated with Columbia River water have been shown to concentrate Zn^{65} (3) and may concentrate others of the long-lived radionuclides in Table II to some extent.

Table III compares the concentration of Columbia River radionuclides with those present in the muscle tissue of fish from the river. A small amount of fish in the diet of an individual could serve as a far more important source of these radionuclides than drinking water.

With the exception of the Na^{22} , Cs^{134} and Cs^{137} , the other long-lived radionuclides in Tables II and III are not of world wide distribution at comparable levels. Urine samples from Alaskan Eskimos showed much higher Na^{22} and $Cs^{134-137}$ but did not show any of the other radionuclides listed in Tables II and III.

Our observation of the presence of Na^{22} as a naturally occurring radionuclide in bioassay samples prompted an investigation to determine its fallout rate and also to determine the major food through which it reaches man (4). Na^{22} is produced naturally by the cosmic ray spallation of atmospheric argon and its concentration in air below the tropopause was reported to be about 2 d.p.m. per 10^6 ft³ in 1961.

Our observations of the Na^{22} in air near ground level have shown concentrations an order of magnitude higher than this suggesting that a considerable amount of Na^{22} was introduced into the atmosphere during the past test series (see Figure 10).

In studying the route by which Na^{22} finds its way to man its concentration was compared with that of Cs^{134} and Cs^{137} in foods and bioassay samples. While Cs^{137} is a major fission product, Cs^{134} is present in fallout at a much lower concentration as a result of both fission and neutron activation of stable Cs^{133} .

The measured concentrations of Na^{22} , Cs^{134} and Cs^{137} in several foods and in bioassay measurements along with estimated body burdens based on these bioassay measurements are recorded in Table IV. In addition to the samples obtained locally, Alaskan caribou, moose and reindeer meat, and bioassay samples from Alaskan Eskimos were analyzed and are included in the table. The whole body concentrations of sodium-22 and the cesium radionuclides in Table II were estimated using biological half-lives⁽⁵⁾ of 11 days and 140 days, respectively. It was assumed in this estimate that 90 per cent of the sodium and cesium excreted was in the urine and that the daily urinary excretion rate was 1.5 liters. The major sources of sodium-22 in the foods considered are meat, milk, wheat and fresh water fish with smaller contributions coming from vegetables. The few food samples considered here are certainly not sufficient to give a complete picture of man's sodium-22 intake. However, they indicate the relative importance of different foods and suggest that the foods which carry cesium-137 to man also are the main sources of sodium-22. It is interesting to note that the elk tissue from Quinault, Washington has sodium-22, cesium-134 and cesium-137 concentrations which are comparable with those in Alaskan caribou. Obviously, a small amount of this meat in the diet could provide the major source of these radionuclides.

The ratios of sodium-22 and cesium-134 to cesium-137 in the Alaskan caribou flesh samples taken just prior to and following the 1961-62 test series show

a considerable difference. The sodium-22 to cesium-137 ratios in samples taken after the tests (July, 1963) were about ten-fold higher than in samples taken just prior to the tests, while the cesium-134 to cesium-137 ratios were a factor of 4 lower. This would suggest that during the past test series considerable amounts of sodium-22 were generated. It would also indicate that the major injection of cesium-134 into the atmosphere occurred in tests prior to 1961-62 series.

It is evident from Table IV that the ratio of Cs^{134} to Cs^{137} in Columbia River fish is much higher than that in the other foods listed. This is due to the fact that Cs^{134} is produced independently in river water during reactor cooling by an (n,γ) reaction on inert Cs^{133} .

Summary

The direct bioassay measurement of radionuclides in urine samples by newly developed multidimensional gamma-ray spectrometric techniques has proven to be an extremely sensitive method for estimating radionuclide body burdens. The interference from natural radioactive potassium is eliminated for most radionuclides which decay by emission of two or more gamma-rays in cascade. The method is far more sensitive than present whole body counting methods for the determination of body burdens of many radionuclides. In addition, the urine bioassay removes the uncertainty as to whether the radionuclide is in the blood stream or the gastro-intestinal tract.

The multidimensional analysis is also more sensitive than many procedures which require both chemical separation and instrumental analysis, yet it provides a complete spectrum and a coincidence spectrum of the gamma radiation leaving a sample. Through use of these techniques the movement of many radionuclides at their present level can be traced through the food chain to man and their uptake and excretion rates can be measured.

Acknowledgement

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TABLE I

Coincidence Gamma-Rays Used in the Measurement of Certain Radionuclides
in Bioassay Samples.

Radionuclide	Gamma-Ray Energies, Mev
Na ²⁴	1.38, 2.75
Cu ⁶⁴	0.51, 0.51
As ⁷⁶	0.559, 0.657
Sc ⁴⁶	0.892, 1, 118
Co ⁶⁰	1.17, 1.332
Zn ⁶⁵	0.51, 0.51
Na ²²	1.28, 0.51, 0.51
Cs ¹³⁴	0.605, 0.797

TABLE II

Typical Concentrations of the Radionuclides in Bioassay Samples from
Richland, Washington Compared with the Levels in Drinking Water.

(d. p. m. per liter)			
Radionuclide	Half-life	Urine Samples	Drinking Water
Na ²⁴	15 hr.	20	3000
Cu ⁶⁴	12.8 hr.	2	1500
As ⁷⁶	26.5 hr.	40	500
Sc ⁴⁶	84 day	2	20*
Zn ⁶⁵	245 day	12	200*
Co ⁶⁰	5.27 yr.	~ 0.06**	3*
Cs ¹³⁴	2.1 yr.	0.6	0.05*
Cs ¹³⁷	30 yr.	150	1*
Na ²²	2.58 yr.	1.5	<0.02*

* Columbia River Water Concentrations

** Estimated from a 7,000 minute count on a large composite sample.

TABLE III

Comparison of the Concentrations of Long-lived Radionuclides in the
Columbia River with those present in Columbia River Fish.

d. p. m. per kg.			
Radionuclide	Columbia River	Pass *	Channel ** Catfish
Sc ⁴⁶	20	66	12
Co ⁶⁰	3	136	105
Zn ⁶⁵	200	36,500	26,300
Na ²²	<0.02	8.3	0.83
Cs ¹³⁴	0.05	120	10.9
Cs ¹³⁷	1	2,400	190

* Collected April 2, 1964

**Collected April 16, 1964

FIGURE 1

DETECTION SYSTEM FOR MULTIDIMENSIONAL GAMMA RAY
SPECTROMETER

Figure 2
 Cu^{64} SPECTRA

Figure 3
Co⁶⁰ SPECTRA

FIGURE 4

BACKGROUND MEASUREMENTS OF A 4 INCH THICK
BY 6 INCH DIAMETER CRYSTAL IN A 4 INCH LEAD SHIELD

Channel Numbers of Both X and Y Axes

FIGURE 5

BACKGROUND MEASUREMENTS ON A DIAGONAL FROM
0 TO 3 MEV WITH DIFFERENT COINCIDENCE AND
ABSORBER CONDITIONS

FIGURE 6
COMPARISON OF THE BACKGROUND COUNTING RATES OF
A SINGLE CRYSTAL WITH THAT OF THE TWO CRYSTAL
MULTIDIMENSIONAL DETECTOR SYSTEM.

FIGURE 7

Zn⁶⁵ BACKSCATTER AT THE TOTAL ABSORPTION (1.112 MEV) ENERGY DIAGONAL IN THE ENERGY-ENERGY PLANE. COUNTS PER CHANNEL ARE NORMALIZED TO 10,000 COUNTS PER CHANNEL IN THE PEAK CHANNELS ON THE AXES.

FIGURE 8
 Co^{60} BACKSCATTER AT THE TOTAL ABSORPTION (2.5 MEV) ENERGY DIAGONAL IN THE ENERGY-ENERGY PLANE, COUNTS PER CHANNEL ARE NORMALIZED TO 10,000 COUNTS PER CHANNEL IN THE TOTAL ABSORPTION PEAK CHANNELS ON THE AXES.

FIGURE 9
TOTAL COUNTING EFFICIENCY AND TOTAL
COINCIDENCE COUNTING EFFICIENCY OF THE
DETECTOR SYSTEM

TABLE IV
SODIUM-22, CESIUM-134 AND CESIUM-137 IN FOODS, BIOASSAY SAMPLES AND PEOPLE

Western United States								Alaska							
Sample	Location	Date Obtained	d/m per kg			$\frac{Na^{22}}{Cs^{137}} \times 100$	$\frac{Cs^{134}}{Cs^{137}} \times 100$	Sample	Location	Date Obtained	d/m per kg			$\frac{Na^{22}}{Cs^{137}} \times 100$	$\frac{Cs^{134}}{Cs^{137}} \times 100$
			Na ²²	Cs ¹³⁴	Cs ¹³⁷						Na ²²	Cs ¹³⁴	Cs ¹³⁷		
Elk	Quinault, Wn	5/64	74.4	9.19	6770	1.10	0.14	Caribou Meat	Near Kotzebue, Alaska	7/63	180	27.6	8320	2.16	0.33
Bass	Columbia River	4/64	8.3	120	2000	0.41	5.88	Caribou Meat		7/63	89.1	20.9	6000	1.49	0.35
Catfish	Columbia River	4/64	0.83	10.9	190	0.44	5.75	Moose Meat		3/64	58.7		2846	2.06	
Milk	Washington	3/63	6.2	0.76	396	1.57	0.19	Moose Meat		3/64	80.6	~2.3	3670	2.20	~0.06
Wheat	Washington	8/63	3.31	1.86	261	1.27	0.71	Caribou Meat		8/5/61	9.13	33.9	2520	0.36	1.34
Beef	Local Food Store, Washington	5/64	2.47	1.34	1070	0.23	~0.13	Caribou Meat	Anaktuvuk Pass, Alaska	10/9/61	23.0	287	20,600	0.11	1.39
Beef		3/64	0.52	1.00	255	0.20	0.39	Reindeer Meat		8/63	15.6	215	36,000	0.043	0.60
Corn	Oregon	4/64	~0.04		3.8	~1.07		Urine***		1/64	126	16.2	5840	2.16	0.28
Lettuce	California	3/64	0.16		43.6	0.37		Man (Eskimo)**			3427	4620	1,950,000	0.18	0.24
Carrots	California	4/64	~0.07		13.1	~0.53									
Potatoes	Idaho	4/64	0.68		57.6	1.18									
Green Beans	Oregon	4/64	~0.20		12.7	~1.57									
Urine Sample*	Washington		1.45	0.56	144	1.01	0.39								
Man**	Washington	11/63	39.5	160	48,000	0.082	0.34								

* Richland, Washington, Composite from Several Individuals

** These Values are Estimated Whole Body Burdens for Sodium-22, Cesium-134 and Cesium-137

*** Composite from 2 Alaskan Eskimos

✓

APPLICATION OF TERTIARY AMINE EXTRACTION
TO THE DETERMINATION OF URANIUM
IN BIOLOGICAL MATERIALS

by

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INTRODUCTION

Current research at the Hanford Laboratories concerning the fate of inhaled uranium ore dust and the radioactive uranium daughter products has led to the development of sensitive radiochemical procedures for the determination of uranium in biological materials. Since the intent of the study is to determine the solubility of the uranium ore dust in the lung and the resultant deposition of uranium and its daughter products in the various organs of the body, procedures for the sequential analysis of the radioelements present are required. Of particular interest in this program is the analysis of the biological material for both uranium and thorium. In addition to this application, the radiochemical procedures developed are suitable for the analysis of urinary excreta from personnel involved in the processing of irradiated thorium, or individuals engaged in the investigation of U^{232} as a possible power source.

Liquid anion exchange using long chain tertiary amines has been shown to be an effective means of separating actinides from various mineral acid solutions⁽¹⁾ and showed promise as a method of analyzing biological samples for these radio-nuclides. This paper discusses the adaptation of tertiary amine extraction to the determination of uranium in tissue and urine.

EXPERIMENTAL

Reagents

The tertiary amine chosen for this study was Alamine-336, Tricaprylyl Amine,

* General Electric Company, Richland, Washington. Work performed under Contract No. AT(45-1)-1350 for the U. S. Atomic Energy Commission.

purchased from the General Mills Company of Kankakee, Illinois. Non-aqueous titration of the amine with dilute hydrochloric acid gave an equivalent weight of 384.0 g compared to 392.0 as specified for pure Alamine-336 by the manufacturer. Purification⁽²⁾ of a portion of the amine to remove primary and secondary amines showed the concentration of these constituents to be less than 2% and therefore the amine was used without purification. All other reagents used in the investigation were analytical reagent grade. All water used was doubly distilled.

Sample Preparation

Two methods of sample preparation were employed in the analysis of tissue specimens for uranium. One method consisted of complete oxidation of the carbonaceous material using ionized and atomic oxygen as oxidants. The apparatus used in this method was a Tracerlab Low Temperature Asher (LTA-500) which produces the ionized and atomic oxygen by passing a stream of oxygen gas through a high frequency electromagnetic field. Temperatures during the ashing procedure are normally below 150° C., thus minimizing the formation of refractory actinide compounds, principally those of thorium. Reagent contamination resulting from wet ashing with mineral acids is also minimized. Ashing of tissue samples ranging in weight from 1-10 g wet weight required overnight treatment to insure total destruction of the organic material present. Dissolution of the resulting ash was accomplished with 6 M nitric acid.

A mixture of concentrated nitric, sulfuric and perchloric acids was used in the wet digestion of tissue specimens, since this medium has been successfully applied in the dissolution of other biological samples⁽³⁾. Digestion in this media was normally complete within one hour using the quantities of tissue mentioned above.

In the case of urine specimens, 100 milliliters of sample were acidified with 50 milliliters of concentrated nitric acid, and the resultant solution boiled to an approximate 10 milliliter volume.

Extraction Media

In choosing a suitable aqueous medium from which to perform the amine extraction of uranium, several possibilities could be immediately eliminated. Amine extraction of uranium from urine using hydrochloric acid as the aqueous phase has been reported⁽⁴⁾. Hydrochloric acid media have the advantage of separating uranium and thorium quantitatively from one another but suffers from a lack of selectivity for uranium because of the extraction of several inorganic constituents present in tissue and urine. Table I shows a compilation of these inorganic constituents as tabulated for standard man⁽⁵⁾. Copper, iron, and zinc all form anionic complexes with chloride ion and would be quantitatively extracted by the tertiary amine and as such would interfere in the radiometric determination of uranium by increasing the amount of inert material on the counting planchet. Extraction of uranium from nitric acid systems increases selectivity but efficient extraction of uranium does not occur from this medium⁽⁶⁾. Extraction of hexavalent uranium from acetate systems also increases selectivity, but two extractions of the aqueous medium must be performed if uranium recovery is to be maintained above 90%⁽⁷⁾. Finally, extraction of actinides from heavily salted aluminum nitrate solutions has been reported⁽⁸⁾, and this medium appeared to offer the most suitable matrix from which to perform the amine extraction.

Extraction

Urine. Since urine contains relatively large amounts of calcium and phosphorus (as phosphates) an alkaline earth phosphate precipitate was used as a non-isotopic carrier for the uranium. In order to optimize the extraction procedure it was necessary to experimentally determine what concentration of amine solution was required to provide the greatest recovery of uranium. Using the detailed procedure outlined in Appendix A, U^{233} was recovered from 100 milliliters of ashed urine by extraction of the acid deficient aluminum nitrate solution containing the uranium with various concentrations of amine solutions. Figure 1 indicates no change in the percentage of the uranium recovered using solutions ranging in concentration from 10 to 20% w/v of the amine in xylene. A 10% w/v Alamine-336 in xylene solution was chosen for the standard extraction procedure since better phase behavior resulted at this rather than higher concentrations of amine.

Tissue. An experiment similar to the one described above was performed for tissue specimens. The results were identical to those obtained for urine, i.e., a 10% w/v solution of Alamine-336 in xylene provided the optimum concentration of amine solution for uranium extraction of the resulting aluminum nitrate solution.

Spectrophotometric measurements of the organic phase following extraction of macro quantities of uranium from the aluminum nitrate solution are compared in Figure 2 with the spectrum obtained from the salt $[(Et)_4N]UO_2(NO_3)_3$. The spectra serve to identify the extracted species as the $UO_2(NO_3)^-$ complex.

RESULTS OBTAINED

The detailed tertiary amine extraction procedure outlined in Appendix A has been tested on high grade uranium ore, and on tissue and urine samples containing both spiked and metabolized uranium isotopes. Table II shows the uranium recoveries observed and the excellent precision which can be obtained using the procedure.

TABLE I
INORGANIC ELEMENTS IN TISSUES AND ORGANS OF MAN

($\mu\text{g/g}$ wet tissue)						
<u>Elements</u>	<u>Lung</u>	<u>Muscle</u>	<u>Bone</u>	<u>Liver</u>	<u>Kidney</u>	<u>Urine</u> (mg/1400 ml)
Ca	130	74	148,000	70	115	200
Cu	1.3	1.4	.6	8.6	2.9	---
Fe	300	44	115	185	76	1-5
Zn	14	43	66	46	48	---
P	1110	1200	80,000	2700	1700	1100

TABLE II
TERTIARY AMINE EXTRACTION RESULTS
FOR SEPARATING URANIUM FROM WET ASHED AND
DRY ASHED BIOLOGICAL SAMPLES

<u>Sample</u>	<u>Ashing Method</u>	<u>Isotopes Used</u>	<u>Uranium Recovery (%)</u>
Rat Lung	Dry	$\text{U}^{233}, \text{U}^{235}$	97 ± 2
Rat Lung	Wet	$\text{U}^{233}, \text{U}^{235}$	90 ± 2
Rat Urine	Wet	U^{233}	93 ± 2
Human Urine	Wet	$\text{U}^{233}, \text{U}^{235}, \text{U}^{238}$	93 ± 2
Uranium Ore*	Acid Digestion HF Evaporation Amine Extraction	U^{238}	100 ± 1

* Uranium ore was analyzed by standard chemical methods and the uranium determined gravimetrically. Amine extractions were performed on weighed ore samples which had been solubilized by acid digestions. Aliquots of the back extractant were taken for coulometric titration and the concentration of uranium in the ore as determined from the amine extractions were compared with the values obtained from the gravimetric analysis.

RECOVERY OF U^{233} FROM SPIKED URINE SPECIMENS
USING STANDARD EXTRACTION PROCEDURE WITH
VARIOUS CONCENTRATIONS OF ALAMINE-336 IN
XYLENE

Figure 1

ABSORPTION SPECTRA OF URANIUM (VI)

- A. Alamine-336/Xylene Organic Phase Following Extraction of Macroquantities of Uranium VI from Acid Deficient Aluminum Nitrate Solution.
- B. Tetraethylammonium Trinitratodioxouranate (VI) in Nitromethane.

NOTE: Absorbances = 0 at Intercepts with Right Ordinate.

Figure 2

The uranium recoveries for the biological samples are the averages of ten separate analyses and the deviations reported are the standard deviations from these averages.

The lower recoveries resulting from the wet ashing procedure for tissue can be attributed to traces of perchloric acid which are carried up to the extraction step. The perchlorate ion has a large affinity for the organic phase and significantly reduces actinide distribution coefficients⁽⁹⁾.

Decontamination of uranium from its daughter products is excellent as is evidenced from Figure 3 which shows the alpha energy spectrum of a high grade uranium ore in secular equilibrium with its daughter products and Figure 4 which shows the alpha energy spectrum of the uranium which has been separated from the same ore by the amine extraction procedure. The resolution of the U^{234} peak is between 4 - 5% (full width at half maximum). Figure 5 shows the alpha energy spectrum of U^{233} which has been separated from urine. Again the resolution is measured as 5%.

The recovery of the major inorganic constituents in tissue and urine are presented in Table III. The inextractability of these elements accounts for the resolution obtained in alpha energy spectra of the recovered uranium. The weight increase on the counting planchets following evaporation of the acetic-nitric acid concentrate range in value from 0.8 to 1.0 milligram. These data are significant in that iron (III) can be used as a non-isotopic carrier for hexavalent uranium in samples where there is insufficient calcium phosphate to serve this purpose.

Table IV shows the excellent decontamination of uranium from other actinides one can obtain using a slight modification of the standard extraction procedure outlined in Appendix A.

ALPHA ENERGY SPECTRUM OF 300 MICRO-GRAMS OF FINELY GROUND URANIUM ORE AS MEASURED IN A FRISCH GRID CHAMBER

Figure 3

ALPHA ENERGY SPECTRUM OF URANIUM
SEPARATED FROM HIGH GRADE URANIUM ORE

Figure 4

ALPHA ENERGY SPECTRUM OF U^{233}
SEPARATED FROM URINE

Figure 5

TABLE III

RECOVERY OF MAJOR INORGANIC ELEMENTS PRESENT IN TISSUE AND URINE
USING STANDARD EXTRACTION PROCEDURE

<u>Element</u>	<u>% Tracer Recovered*</u>
Ca	0
Cu	< 0.01
Fe	< 0.01
Zn	< 0.02

* Each element was examined at both tracer and milligram levels.
No difference was observed in the per cent recovered.

TABLE IV

RECOVERY OF ACTINIDES FROM ASHED URINE
USING THE MODIFIED AMINE EXTRACTION PROCEDURE

<u>Radionuclide</u>	<u>% Tracer Recovered</u>
U ²³³	93 ± 2
Pu ²³⁹	0.5
Am ²⁴¹	< 0.05
Np ²³⁷	0.4
Th ²³⁰	< 0.01

DISCUSSION

The results of the present investigation provide a method of determining uranium in biological materials which has certain advantages over existing methods of analysis for this radionuclide. Rapid qualitative analysis of ashed urine for actinides can be accomplished following extraction by simply plating the organic phase on a counting planchet, drying and flaming the residue, and counting the sample in a suitable alpha energy analyzer. This method of source preparation yields alpha energy peaks with resolutions of 4-5% and readily permits the identification of Pu^{239} , Np^{237} , U^{238} , and Th^{232} if they are present in the sample. Furthermore, in the analysis of urinary excreta of personnel involved in the processing of irradiated thorium, the resolution thus obtained allows identification of Th^{232} , U^{232} , and U^{233} , all of which might be present in the urine of these individuals following an inadvertent exposure.

Aliquots of the organic phase and the acetic-nitric acid concentrate can be used in the fluorometric determination of these solutions for U^{238} . Table V shows the results obtained in the analysis of 100 milliliters of spiked urine using the standard extraction procedure. The results reported are the averages of two aliquots taken from each sample. The excellent agreement obtained in the analysis of the acetic-nitric acid concentrate is more apparent than real, since duplicates differed by approximately 10 per cent.

It is always of interest to calculate what quantities of a radionuclide can be detected by a particular radiochemical procedure. If 0.1 milliliter aliquots of the acetic-nitric acid concentrate or organic phase are taken for fluorometric analyses of U^{238} , 10 μg of U^{238} /liter of urine can be reliably detected using a sample size of 100 milliliters. The detection limit in the analysis of urine for U^{233} will of course depend on the type of alpha detector used in counting the sample.

Table VI presents calculated sensitivity limits for the most common alpha counters currently in use. Using the data of Bernard and Struxness⁽¹⁰⁾, for the urinary excretion of uranium, it would be possible to detect 10 per cent of a maximum permissible body burden of soluble U^{233} 90 days following acute exposure.

Analysis of urinary excreta using tertiary amines offers a method of sequentially analyzing this media for those actinides of major interest to the health physicist. For the procedure outlined for excreta all tetravalent and hexavalent isotopes of Th, Np, U, and Pu are extracted into the organic phase. With the proper choice of wash solution, each of these elements can be removed from the organic phase and determined separately. The versatility of amine extraction and the precision attainable in the analysis of the actinides should stimulate interest in its application to the determination of these radionuclides in biological systems.

TABLE V

FLUOROMETRIC ANALYSES OF URANIUM SEPARATED FROM URINE
BY THE STANDARD EXTRACTION PROCEDURE*

Sample	Phase Analyzed	$\mu\text{g U}^{238}$ Added	$\mu\text{g U}^{238}$ Found
1	Organic	1.00	1.04
2	"	1.00	1.08
3	"	1.00	1.08
4	"	1.00	1.04
5	"	2.00	2.12
6	"	2.00	2.18
7	Acetic-Nitric Acid	1.00	1.03
8	"	2.00	1.99
9	"	3.00	3.03

* Each urine specimen was 100 milliliters in volume.

TABLE VI

DETECTION LIMITS FOR THE ANALYSIS OF URINE CONTAINING U^{233}

Instrument	Average Background	Detection Limit (99% Confidence Level)
Proportional Counter	0.05 CPM	8 DPM/liter
ZnS Scintillation Counter	0.01 CPM	3 DPM/liter
Frisch Grid Ion Chamber (300 kev photopeak)	0.006 CPM	3 DPM/liter

APPENDIX A

Procedures

A. Sample Preparation

Tissue. Preparation of tissue samples for uranium analyses can be accomplished by either dry or wet ashing procedures. In the development of the radiochemical procedure that follows, dry ashing was accomplished by oxidation with an atomic oxygen furnace. The sample is first dried either under a heat lamp or in a freeze dryer, and the sample subsequently oxidized in the oxygen furnace for approximately 12 hours or overnight. The resulting ash is dissolved in 2 milliliters of 6 M HNO_3 and transferred to a 60 milliliter separatory funnel using 10 milliliters of 2.8 M $\text{Al}(\text{NO}_3)_3$ which is 1 N acid deficient.

Wet digestion of tissue samples can be accomplished by a mixture of concentrated nitric, sulfuric and perchloric acids. For tissue samples of ten grams or less wet weight, 50 milliliters of concentrated nitric, 5 milliliters concentrated perchloric and 5 milliliters of concentrated sulfuric acid are adequate to digest the organic materials present. The digestions should be carried out on a hotplate at medium heat in covered beakers equipped with bumping rods, since the sample effervesces at several points during the digestion. Dissolution is continued until effervescence has ceased and the great majority of perchloric acid has been removed. The time required for digestion is normally 1-1/2 - 2 hours. The sample is cooled, transferred to a lusteroid tube with thirty milliliters of pH = 2.0 nitric acid from a wash bottle. Twenty milligrams of iron carrier is then added and the solution made basic to precipitate ferric hydroxide which carries uranium and other actinides. The sample is centrifuged, the supernate decanted by suction and the precipitate washed with 10 milliliters of H_2O . The supernate is again decanted by suction, the precipitate dissolved in 2 milliliters of 8 M HNO_3

and the resulting solution transferred to a 60 milliliter separatory funnel using 10 milliliters of 2.8 M $\text{Al}(\text{NO}_3)_3$ which is 1 N acid deficient.

Urine. One hundred milliliters of urine and 50 milliliters of concentrated HNO_3 acid are taken to small volume (~ 5 milliliters) in a 250 milliliter beaker which is covered with a watch glass and equipped with a bumping rod. The sample is cooled, transferred to a 100 milliliter tusteroid tube using 30 milliliters of $\text{pH} = 2.0$ HNO_3 from a wash bottle and the solution made basic by the addition of 20 milliliters of concentrated NH_4OH . The resulting alkaline earth phosphate precipitate carries uranium and any Th, Np and Pu that may be present in the sample. The supernate is decanted by suction and the precipitate washed once with 10 milliliters of distilled water. Following centrifugation and decantation of the supernate by suction, the phosphate precipitate is dissolved in 2 milliliters of 8 M HNO_3 and transferred to a 60 milliliter separatory funnel using 10 milliliters of the above mentioned $\text{Al}(\text{NO}_3)_3$ solution.

B. Extraction

The tetra and hexavalent actinides are extracted from the aluminum nitrate solution by 10 milliliters of 10% w/v Alamine-336 in xylene by contacting these two solutions on a mechanical shaker at maximum agitation for five minutes. Phase separation is accomplished by centrifugation and the aqueous layer is discarded. The organic phase is scrubbed once with 5 milliliters of fresh $\text{Al}(\text{NO}_3)_3$ solution which is also discarded following centrifugation. If the sample is to be analyzed for U^{238} an aliquot of the organic phase can be taken for fluorometric analyses (normally 100 μ liters). If neptunium and plutonium are known to be absent from the sample, the organic phase is washed twice with 10 milliliter portions of 7 M HCl which serves to

strip any thorium and trivalent rare earths or trivalent actinides that might be present in the sample. The uranium is then stripped from the organic phase by two 10 milliliter washes with 0.1 M HNO_3 . The back extractant is evaporated to dryness and the small residue dissolved in 5 milliliters of a 20:1 concentrated $\text{CH}_3\text{COOH-HNO}_3$ solution. The solution is reduced in volume to 2 milliliters by evaporation under a heat lamp and the resulting solution plated on a 1-1/2 inch stainless steel counting planchet. The beaker is rinsed with two 2-milliliter washes using the acetic-nitric acid concentrate and the washes are added to the planchet. Following flaming to a dull red heat the sample is then ready for either total alpha counting or alpha energy analysis. Alternatively, the beaker can be rinsed with several washes using heated acetic-nitric acid concentrate, the resulting solution diluted to a known volume and an aliquot taken for the fluorometric determination of U^{238} and an aliquot plated for alpha energy analysis.

C. Modified Procedure

If neptunium and plutonium are suspected of being present in the sample they can be removed by scrubbing the organic phase once with a 10 milliliter 7.0 M HCl - 0.5 M HF wash followed by a 10 milliliter 7.0 M HCl - 0.1 M HI wash. The uranium can then be stripped with 0.1 M HNO_3 according to the regular procedure. The wash solutions containing the Np and Pu can then be processed to recover these isotopes thus enabling sequential analysis for these actinides.

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ABSTRACT

DETERMINATION OF RADIOISOTOPES OF CERIUM, BARIUM, LANTHANUM, AND NEPTUNIUM AFTER SEPARATION BY BARIUM SULFATE

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Radioactive isotopes of cerium, barium, lanthanum and neptunium in carrier-free quantities are separated quantitatively from most other elements by precipitation with barium sulfate from strong sulfuric acid solutions containing potassium salts and hydrogen peroxide. Neptunium is removed from the barium sulfate precipitate by reprecipitating the latter from concentrated sulfuric acid in the presence of permanganate. The barium sulfate is then dissolved in alkaline DTPA-TEA solution and radiocerium is precipitated in the presence of cerium carrier by addition of hydrogen peroxide. The filtrate is acidified with acetic acid which reprecipitates barium as the sulfate and leaves lanthanum in the aqueous solution. Both lanthanum and neptunium can be reprecipitated from their respective solutions by addition of potassium salts, hydrogen peroxide and barium chloride. The individual isotopes are then determined preferably by gamma spectrometry although gross beta or gamma counting can be used in many cases. Recovery of each isotope is better than 99% making determination of chemical yields unnecessary. The entire separation requires less than two hours. The procedure has been applied to air dusts, water and many kinds of mineralogical and biological materials.

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Figure 1.
DOCTOR

INFORMED
FURNACE

John Doe

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INDUCTION COIL

~~Induction Coil~~

Induction Coil