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PROCEEDINGS OF
BIO-ASSAY AND ANALYTICAL MEETING

OCTOBER 6 - 7, 1955

Edited by

Reynold L. Hoover

FEED MATERIALS PRODUCTION CENTER
NATIONAL LEAD COMPANY
OF OHIO

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PROCEEDINGS OF
BIO-ASSAY AND ANALYTICAL CHEMISTRY
MEETING

OCTOBER 6 AND 7, 1955

Edited by
Reynold L. Hoover

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BIO-ASSAY AND ANALYTICAL CHEMISTRY MEETING

OBJECTIVES

The Bio-Assay and Analytical Chemistry Meeting was set up to accomplish the following objectives:

1. To bring everyone up-to-date on some of the latest developments in the field of bio-assay.
2. To enable all persons actively engaged in the field of bio-assay and analytical chemistry to discuss mutual problems.
3. To standardize some of the procedures commonly used by the various laboratories.
4. To enable each laboratory to become familiar with procedures used elsewhere.
5. To plan future meetings of this type.

It is the desire of the National Lead Company of Ohio that each of the representatives of the other installations leave the meeting with the feeling that all of these objectives have been fulfilled.

AGENDA

Thursday, October 6, 1955

Conference Room - Technical Laboratory Building

Presiding: Mr. R. L. Hoover, Head
Analytical Laboratory Department
Health & Safety Division
National Lead Company of Ohio

- 8:00 Transportation provided from Netherland Plaza Hotel,
Cincinnati, Ohio
- 8:45 Registration at Administration Building, National Lead Company
of Ohio

Session I

- 9:00 Welcome - Mr. G. W. Wunder, Plant Manager,
National Lead Company of Ohio, Cincinnati, Ohio
- 9:15 "General Health Problems Associated with the Handling of Uranium,
Radium, and Thorium" - Dr. J. A. Quigley, Director, Health &
Safety Division, National Lead Company of Ohio, Cincinnati, Ohio
- 10:00 Discussion - "Fluorophotometric Determinations of Uranium in
Urine and Air" - Dr. M. F. Milligan, Staff Member, Los Alamos
Scientific Laboratory, Los Alamos, New Mexico
- 11:15 Intermission
- 11:30 Discussion - "Electrodeposition of Enriched Uranium in Urine" -
Mr. F. Williams, Associate Chemist, Health Physics Division,
Union Carbide Nuclear Company, Oak Ridge, Tennessee
- 12:15 Opportunity to ask questions or go over any information discussed
in Session I.
- 12:30 Lunch

Session II

- 1:30 Discussion - "Determination of Plutonium in Urine" -
Mr. S. M. Sanders, Senior Supervisor, Bio-Assay Laboratory,
Health Physics, Savannah River Plant, Augusta, Georgia
- 2:15 Discussion - "Determination of Fluoride in Water" -
Mr. William L. Lamar, District Chemist, U. S. Geological Survey,
Columbus, Ohio
- 3:00 Intermission
- 3:15 Discussion - "Determination of Tritium in Urine and Water" -
Dr. M. F. Milligan, Staff Member, Los Alamos Scientific Laboratory,
Los Alamos, New Mexico
- 4:15 Opportunity to ask questions or go over any information discussed
in Session II.
- 4:30 Transportation to downtown Cincinnati

Friday, October 7, 1955

Conference Room - Technical Laboratory Building

Presiding: Mr. R. L. Hoover, Head
Analytical Laboratory Department
Health & Safety Division
National Lead Company of Ohio

- 8:00 Transportation provided from Netherland Plaza Hotel,
Cincinnati, Ohio
- 8:45 Registration at Administration Building, National Lead Company
of Ohio

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Session III

- 9:00 Discussion - "Analysis of Urine for Thorium" -
Dr. J. M. Nielsen, Head, Methods Unit, Radiological Sciences
Department, Hanford Atomic Products Operation
- 10:45 Intermission
- 11:00 Discussion - "Determination of Mercury in Urine and Air" -
Mr. Evan Campbell, Staff Member, Los Alamos Scientific Laboratory,
Los Alamos, New Mexico
- 11:45 Discussion - "The Natural Radioactivity of Man" -
Dr. John Hursh, Associate Professor Radiation Biology, University
of Rochester School of Medicine and Dentistry, Rochester, New York
- 12:30 Lunch

Session IV

- 1:15 Discussion - "Determination of Micromicrogram Quantities of
Radium" - Dr. Jacob Sedlet, Associate Chemist, Analytical
Laboratory, Industrial Hygiene & Safety Division, Argonne National
Laboratory, Lemont, Illinois
- 2:00 Discussion - "Program Suggestions and Plans for Future Meetings
of this Type"
- 2:30 Discussion - "Counting Techniques and Instrumentation" -
Mr. R. L. Hoover, Head, Analytical Laboratory Department,
Health & Safety Division, National Lead Company of Ohio,
Cincinnati, Ohio
- 3:00 Opportunity to ask questions or go over any information discussed
in Sessions III and IV.
- 3:15 Meeting will be closed. Dr. J. A. Quigley, Director,
Health & Safety Division, National Lead Company of Ohio,
Cincinnati, Ohio
- 3:30 Transportation to downtown Cincinnati, to airport and to railroad
station

WELCOME

Mr. G. W. Wunder, Plant Manager
National Lead Company of Ohio
Cincinnati, Ohio

The National Lead Company of Ohio regards it as a privilege to serve as your host for the first Bio-Assay and Analytical Chemistry Meeting during these few days, and I wish to welcome you to the Fernald Feed Materials Production Center.

Those of us who are involved in feed material production have a keen interest in the research and over-all program of you who are engaged in the field of Bio-Assay and Analytical Chemistry. It is largely through your efforts that the health of those who work with radioactivity is maintained.

I know that by your presence here and your participation that this meeting will be informative and that the objectives set forth for your meeting will be accomplished.

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INTRODUCTION

The Bio-Assay and Analytical Chemistry Meeting was sponsored by the Analytical Laboratory Department, Health and Safety Division, of the National Lead Company of Ohio, with the cooperation of the Atomic Energy Commission.

The meeting was limited in attendance to those individuals who were engaged in the field of bio-assay and analytical chemistry so that the maximum amount of discussion and group participation could be achieved.

Two of the major outgrowths of the meeting were: (1) the establishment of a group to investigate the standardization of methods and (2) further plans for annual meetings of this type.

Three of the papers presented at the two-day meeting were omitted from this report:

"General Health Problems Associated with the Handling of Uranium, Radium, and Thorium", by Dr. J. A. Quigley (Director, Health & Safety Division, National Lead Company of Ohio) is classified.

"Determination of Plutonium in Urine", by Mr. S. M. Sanders (Senior Supervisor, Bio-Assay Laboratory, Health Physics, Savannah River Plant) also is classified but is available to Q-cleared personnel as Document No. DPSP-55-596.

"Analysis of Urine for Thorium", by Mr. J. M. Neilsen (Methods Unit, Radiological Sciences Department, Hanford Atomic Products Operation) has been omitted in order to give first publication rights to "Analytical Chemistry".

FLUOROPHOTOMETRIC DETERMINATIONS OF URANIUM IN URINE AND AIR

by Morris F. Milligan, Staff Member,
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

PART I

A SIMPLE D-C FLUOROPHOTOMETER FOR DETECTING URANIUM⁽¹⁾

The fluorescence of uranium under ultraviolet light (first recorded by Stokes in 1852), using a uranium salt fused with sodium fluoride, has been used recently for detecting uranium in urine. Although the instrument described here was developed for this purpose, it was anticipated that something could be learned about the factors influencing sensitivity, i.e.,

1. The effects of aging and variations of the ultraviolet light.
2. The effect of various methods of preparing the sodium fluoride buttons.
3. The sensitivity of various methods of electronic detection.

To isolate and investigate these effects would be an arduous, time-consuming task. It is the purpose of the present investigation to show that a simple workable instrument can be built with the same sensitivity as other methods, and that the practical limit of detection is not bounded by the electronic circuitry.

CIRCUIT

To get some idea of the various effects noted, the electronic circuit must not contribute anomalies. Thus, a simple type of slide-back-voltmeter arrangement was chosen. Because of the low currents from the phototube, it was thought that the d-c technique of Neuman et al.⁽²⁾

could be further improved with an electrometer tube. The circuit chosen, therefore, is of a slide-back-voltmeter electrometer-tube cathode-follower type that has been used extensively in this laboratory for some years.⁽³⁾

PROCEDURE

In general, the procedure for preparing samples is similar to that of Neuman et al.⁽²⁾ and Price, Ferretti, and Schwartz.⁽⁴⁾

The platinum dishes containing the sample are flamed over an open gas-air burner, the flame of which is kept constant with manometers on both the gas and air lines. The 1-min fusion time starts when the last bit of sodium fluoride melts. At the start of timing, the flame is moved slightly to the side to allow the flux to spread evenly over the dish, then returned so that the dish remains over the center of the burner. A 5-min time lapse should be allowed before returning the dishes to the porcelain plate, to permit uniform freezing. If air drafts are kept at a minimum, better fusions are obtained. Too severe drafts during fusion cause the flux to turn yellow, which lowers the fluorescence. Sometimes refusion of the yellow flux clears it to the usual white crystals.

The measurement of the amount of uranium is comparative so that a standard stock solution is made, plotting grams against vernier readings. After dissolving 2.11 g uranyl nitrate hexahydrate in one liter of 2N nitric acid, a series of 1-to-10 dilutions is made to obtain a final concentration of 0.01 µg uranium per milliliter of solution. Volumes of 25, 50, 75 and 100 microliters (or 20, 50, etc.) are used

and the curve plotted with these points. Separate graphs have to be made for higher concentrations measured on a less sensitive scale. To check for drift, blank readings are taken between each set of unknowns and the difference averaged in the calculations. Blank spike readings provide a check on the possible contamination of blanks and also check the instrument.

In calculations, the blank readings are subtracted from those of the unknowns to give the exact vernier reading of the sample to be read on the graph. Readings from the graph are in grams per 100 microliters. Urine samples are reported in micrograms uranium per liter of urine, and air samples in total micrograms per sample.

SENSITIVITY FACTORS

With this experience, it is possible to draw some general conclusions as to the nature of the instrument and the procedure.

Effects of Aging and Variations of U-V Light Source

In practice, the light source is turned on on Monday morning and turned off the following Friday afternoon. A new bulb shows an increase in intensity of approximately 10 per cent in a period of two weeks, after which it remains at a constant intensity for several months; thereafter it gradually declines. This general behavior is independent of voltage-regulating transformers.

There are wide variations in intensity between lamps from various manufacturers, but in general they all show the same behavior.

We believe this behavior is attributable to the light source for the following reasons: It is very easy to check the sensitivity of the

electronic circuit inasmuch as a given change of duodial setting should always deflect the galvanometer a given number of divisions. This effect was always checked with a blank that was made from the same lot of C.P. sodium fluoride.

Effects of NaF Button Preparation

Experience has shown that the preparation of the sodium fluoride buttons is the most critical operation in the whole method. The buttons should crystallize as uniformly as possible to a white color; occasionally brown spots have appeared that affect the sensitivity, but the addition of 10 per cent sodium carbonate minimizes this condition.

There are wide variations in the backgrounds of sodium fluoride, although spectrographic analysis of various samples has not shown conclusive reasons for this. At present the method consists of trying sodium fluoride from various sources and selecting the samples with the lowest background. An acceptable batch of sodium fluoride on scale 2 of this instrument gives a reading of 22-44 divisions on the duodial.

The cleaning of the platinum dishes is important because of the sensitivity. The dishes are first cleaned in concentrated sulfuric acid in a large platinum dish until all the flux dissolves, then rinsed well and boiled in 1:1 hydrochloric acid, followed by repeated rinsings and boilings in concentrated nitric acid. Clean dishes should be kept in concentrated nitric acid all the time, and before using brought to a boil and rinsed at least three times with distilled water.

The fluorescence depends on the method of cooling the buttons. The best practice is to move the flame to one side rather than move the

dish. Some preliminary experiments indicate that fast cooling is better than slow cooling.

Experiments indicate that fluxing and cooling in an argon atmosphere may be desirable. As a result of this process, the buttons were loose in the dish, and it was possible to turn them out.

Sensitivity of the Electronic Detector.

Scale 3 of the present instrument is completely unusable, because the background leakage of the light source and the background of the blank sodium fluoride threw the instrument completely off scale.

With the light off and no blank, grid current is negligible. This is demonstrated by zeroing on the zero position and then switching to scale 3. Any grid current then develops a grid voltage across the 2×10^{11} -ohm resistor and disturbs the zero settings so the grid current may be assumed to be negligible on this scale.

We therefore conclude that, although there is available an increased sensitivity of 20, it is unusable because of the other factors.

As a further check on the sensitivity of our instrument, in 1951, samples were exchanged between Los Alamos and the AEC New York Operations Office. These samples were spiked so that only the originating office knew how much uranium they contained.

The New York Operations instrument is different in the sense that the fluorescent signal is amplified by photomultipliers using modulating techniques.

Table I summarizes the values that Los Alamos found compared with the true value calculated on the basis of a weighed amount of uranium

oxide by the New York Operations Office.

Los Alamos prepared 12 samples by the method previously described; 6 samples contained 10 $\mu\text{g/liter}$ and 6 contained 100 $\mu\text{g/liter}$. Table II summarizes the values that were found on both the Los Alamos and New York instruments.

TABLE I URANIUM DETERMINATIONS MADE ON NYO SAMPLES

URANIUM CONCENTRATIONS ($\mu\text{g/liter}$)		
<u>SAMPLE NO.</u>	<u>LOS ALAMOS RESULTS</u>	<u>NEW YORK OPERATIONS "TRUE" VALUES</u>
1	82	98
2	51	54
3	11	16
4	11	6
5	0	0
6	11	26
7	34	46
8	69	76
9	0	2
10	0	8
11	25	34
12	51	64

TABLE II COMPARISON OF LOS ALAMOS AND NYO INSTRUMENTS

URANIUM CONCENTRATION ($\mu\text{g/liter}$)			
<u>SAMPLE NO.</u>	<u>STANDARD SOLUTION</u>	<u>LOS ALAMOS</u>	<u>NYO</u>
1	10	8	13
2	10	10	14
3	10	10	11
4	10	10	11
5	10	10	8
6	10	9	12
7	100	101	99
8	100	101	91
9	100	101	99
10	100	101	105
11	100	101	96
12	100	99	91

Inasmuch as it is evident that the agreement by these two totally different instruments is quite acceptable, we conclude that this simple instrument has the same sensitivity as other methods of measuring the fluorescence.

PART II

PROCEDURE FOR THE DETERMINATION OF URANIUM IN URINE AND AIR⁽⁵⁾

ABSTRACT

The method is based on the intense yellow-green fluorescence (the principal line of which is reported to be at 555 mμ) produced by traces of uranium fused in sodium fluoride. It is sensitive to concentrations of uranium from 10^{-5} to 5×10^{-10} g per 0.25 g of sodium fluoride with a precision of ± 10 per cent. The tolerance for normal uranium in urine used at LASL is 100 μg per liter.

Air for the determination of uranium is collected by filtration, impingement, or impaction. Glass or molecular filters are usually used and with special extraction methods, HV-70 paper may be used. Ten per cent nitric acid is used as the collecting medium for impinger samples. The air tolerance for normal uranium (tuballoy) used at LASL is 50 μg per cubic meter, which is approximately 66 d/m/M³.

REAGENTS

Concentrated Sulfuric Acid - H_2SO_4 96 per cent, sp gr 1.84

Concentrated Hydrochloric Acid - HCL 36 per cent, sp gr 1.19

Concentrated Nitric Acid - HNO_3 69 per cent, sp gr 1.42

Sodium Fluoride - NaF (AR, powder). The sodium fluoride must be especially pure -- the apparent uranium content cannot exceed 5 parts per 10^{10} by weight of sodium fluoride. The uranium content of sodium fluoride from different bottles of the same lot is usually consistent, but different lots may vary widely. Many different lots, representing several different brands, should be

tested and large amounts of the best lot purchased. In our experience "Baker Analyzed Reagent" from J. T. Baker Chemical Co., Phillipsburg, N. J., has proved, in general, the most satisfactory of several brands tested. The sodium fluoride is tested by running blanks on each lot. Standards are also run on each lot to check the fluorescent response to uranium.

2N Nitric Acid - 128.2 ml of conc. nitric acid is added to 500 ml of distilled water in a liter volumetric flask. Make up to volume with distilled water and mix.

Stock Uranium Standard - 2.11 g of uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ - AR) is placed in a 1-liter volumetric flask and made up to volume with 2N nitric acid. This solution contains 1 mg of uranium per ml. If precise standardization is desired, the uranium in an aliquot of the solution may be converted to uranium oxide (U_3O_8) and weighed.

Standard I - Dilute 1 ml of stock uranium standard to 100 ml with 2N nitric acid. The solution contains 10^{-5} g of uranium per ml.

Standard II - Dilute 10 ml of Standard I to 100 ml with 2N nitric acid. The solution contains 10^{-6} g of uranium per ml.

Standard III - Dilute 10 ml of Standard II to 100 ml with 2N nitric acid. The solution contains 10^{-7} g of uranium per ml.

EQUIPMENT

Platinum Dishes - The dishes are made by the machine shops of LASL from 20-mil platinum.

Micropipettes - Transfer-type pipette in 10, 25, 50, 75 and 100

microliter sizes. These are manufactured by the Microchemical Specialties Co., 1834 University Avenue, Berkeley 3, California. (They are listed in the LASL stock catalog as "pipette, capillary".) These pipettes are boiled twice in conc. nitric acid, rinsed thoroughly in distilled water, boiled in distilled water, and dried in an oven.

Spot Plates - Porcelain spot plates are used to hold and carry the platinum dishes.

Platinum-Tipped Crucible Tongs - 9 inch, used to handle the platinum dishes.

Infrared Lamp - 250 watts, General Electric reflector infrared pyrex heat lamp. Used to dry the platinum dishes and samples.

Fusion Racks - The fusion rack is made of a piece of steel pipe with 2-inch pieces of 4-mm Alundum rod set 1/2-inch apart to support the platinum dishes. The rack should be placed in a spot free from drafts and air currents.

Sodium Fluoride Dispenser - The dispenser is made from an 8-cm length of a 10-ml graduated pipette and a 10.5-cm length of glass rod that slides easily but not loosely inside the tube.

Fisher Blast Burner - Bottled butane is used with compressed air as the fuel gas. The intensity of the flame is adjusted until the flux melts in approximately 1 minute or less (1000-1200°C). High oxygen concentration in the flame should be avoided -- excessive oxygen causes a chemical reaction between the flux and platinum which stains the dish bottoms brown, and sometimes gives the disks

a yellow, orange, or brown color.

Didymium Glasses - Didymium glass glassblower's goggles. These are necessary to observe the molten flux.

Platinum Evaporating Dish - with lip, 4-inch diameter. Used to clean the platinum dishes.

Fluorophotometer - (Designed and built by P-1 Group at LASL).

The light source of the instrument is a CH_4 ultraviolet spot. The light is passed through suitable filters and impinges upon the fused sample in the carrier directly below the source. Emitted light is passed through suitable isolation filters and impinges on the photocell.

The current generated in the photocell is measured with a simple direct current slideback-type voltmeter constructed using electrometer tube techniques. The obvious advantage of this type voltmeter is that any nonlinearity of the electronic circuit is cancelled out. In operation, galvanometer deflection is kept at zero by manipulation of the helipot vernier from which voltage readings are taken.

The over-all linearity of the instrument is evident from inspection of the calibration curves.

PRECAUTIONS

Cleanliness - The most scrupulous attention to cleanliness is necessary for analyses at high sensitivities. All equipment and samples should be protected from atmospheric dust. The dishes should never be touched with fingers from the time of final

rinsing until after the dishes are removed from the instrument.

Platinum-tipped forceps are used to handle the dishes.

Interference - When large amounts of heavy metals are present, as small an aliquot as the uranium concentration will permit is used in order to reduce damage to the platinum dishes.

PROCEDURE

1. Air Samples

(a) Filters - Glass or molecular filters are placed in a beaker, covered with conc. nitric acid and boiled gently for 1 hour or until the volume of acid is reduced to 2-3 ml. The acid is washed quantitatively into a 100-ml volumetric flask and diluted to volume. (If the concentration of uranium is known to be low, a smaller dilution volume is used --- similarly, if the concentration is high, larger dilutions are made.)

(b) Impingers - The contents of the two impingers are combined and washed quantitatively into a 250-ml volumetric flask. Make up to 250 ml with 2N nitric acid.

(c) Impactors - The impactor slides are brought into the laboratory in 50-ml weighing bottles. The bottle (without the lid) is heated carefully over the Fisher blast burner until the resin on the slide is burned off. The bottle and slide are allowed to cool and then covered with 25 ml of conc. nitric acid. The acid is boiled until the volume is reduced to 2-3 ml. The acid is transferred quantitatively into a 10-ml volumetric flask with conc. nitric acid and distilled water and made up to volume with dis-

tilled water. (Larger volumes are used if the uranium concentration is high -- in this case the volume is made up with 2N nitric acid.)

2. Urine Samples

(a) Spot urine samples are collected and brought into the laboratory. Approximately 1 ml of conc. hydrochloric acid is added for every 100 ml of urine. The New York Operations Office of the AEC has found that uranium is not coprecipitated in urines acidified with hydrochloric acid.

3. Fluorophotometer

(a) The ultraviolet light is turned on at 0800 each day and turned off at 1700. If the light should go off for any reason, even momentarily, it must be turned off and allowed to cool for at least 30 minutes before being turned on again. (The light should warm a minimum of 30 minutes before reading samples -- with our present instrument a period of several hours is necessary.) At the same time the on-off switch on the fluorophotometer is turned to the "warm" position for about 30 seconds and then to the "on" position and the galvanometer is turned on. (The galvanometer should also warm for 30 minutes before use.) Set the vernier knob and the sensitivity scale knob at zero. After the lamp has warmed for several hours, the galvanometer should be at zero, the ampere scale should read 1, and the milliampere scale should read 0.5. The "zeroing" should be checked before readings are made. If the galvanometer does not read zero when the vernier is set at zero,

adjust with the sensitivity knob on the back of the instrument.

The zeroing is checked again, and reset if necessary, before turning the instrument off.

To prevent variations due to light leakage, only one position on the present carrier can be used. New carriers should be checked for consistency of reading in all positions.

4. Cleaning Dishes

(a) The dishes are cleaned by heating in conc. sulfuric acid in a platinum evaporating dish until all the flux dissolves. The dishes are rinsed by flooding under the tap (care must be taken to avoid spattering the sulfuric acid). Boil in 1:1 hydrochloric acid for a few minutes. This is followed by repeated rinsings and boiling in conc. nitric acid. Clean dishes are stored in conc. nitric acid until used. Before using, bring the acid to a boil and rinse the dishes at least 3 times with distilled water. Check the dishes for contamination by running fused sodium fluoride blanks in them. If the blank readings are high (indicating a contaminated dish) scour the dish with steel wool and sea sand and repeat the acid cleaning procedure. Continue cleaning until the readings indicate no contamination. The platinum dishes should always be handled with platinum-tipped tongs.

5. The clean platinum dishes are placed on the back of a porcelain spot plate. 0.10 ml of urine or air sample solution is placed in a platinum dish. Each sample is done in triplicate. The sample should be carried through the fusion step without delay to prevent contamination.

6. The dishes with the samples are placed under an infrared lamp to dry. The dishes must be completely dry before the sodium fluoride is added or the disks (the fused sodium fluoride disks) may be discolored.
7. The dried dishes are placed on the fusion rack with platinum-tipped forceps, and ignited over the Fisher blast burner until all the visible material (usually organic material) becomes clear, molten, or volatilized. This reduces disk discoloration and quenching (any process occurring within a fluorescent substance that decreases the observed intensity of fluorescence).
8. Two clean dishes are placed on the fusion rack and treated in the same manner as the samples. These are the "blanks".
9. A small amount of sodium fluoride powder is poured into a Petri dish. The sodium fluoride dispenser is held like a hypodermic syringe and some of the powder is pressed into the tube. A spatula is held flat against the end of the tube and the plunger pushed down to compress the powder into a firm tablet. With the aid of the spatula, the amount of powder is adjusted to give a tablet volume of about 0.25 ml (approximately 0.25 g). The tablet is extruded directly onto the cooled platinum dish.
10. The dishes are fused with the Fisher blast burner. The flux is spread evenly over the bottom of the dish by moving the flame slightly. Fuse for 1 minute -- start timing when the last bit of sodium fluoride melts. During the fusion, keep the flame centered under the center of the dish. Didymium glasses should be worn while fusing.

11. Allow the dishes to cool undisturbed on the fusion rack for approximately 5 minutes. Air drafts should be kept at a minimum. The fused disks should be white and crystalline -- the cooling rate affects the crystalline structure of the disk and hence the fluorescence.
12. The fluorescence of the disks is usually read in the fluorophotometer as soon after fusing as practicable. However, the disk fluorescence seems to be stable for several weeks at LASL if the disks are protected from dust. No "blank rise" (increase in fluorescence due to absorption of moisture) is experienced, due to the low humidity. The blank disks are placed in the first and last position of the five on the carrier and are read before and after each set of samples. If the blank readings change while reading a series of samples, the "zeroing" of the galvanometer should be rechecked.
13. The grams of uranium per sample are determined from the appropriate standard curve (made with the sensitivity scale used for reading the samples) after the vernier reading of the blank has been subtracted from the vernier reading of the sample.

CALCULATIONS

Urine Samples

$$\frac{\text{g U in Sample} \times 10^6 \text{ } \mu\text{g/g} \times 1000 \text{ ml/liter}}{\text{ml sample aliquot}} = \frac{\mu\text{g of uranium per}}{\text{liter of urine}}$$

$$\frac{\text{g U per Sample} \times 10^{10}}{0.10 \text{ ml urine}} = \mu\text{g of uranium per liter of urine}$$

Air Samples

$$\frac{\text{g U in Sample} \times 10^6 \text{ } \mu\text{g/g} \times \text{vol. of air sample solution in ml}}{\text{M}^3 \text{ air collected} \times \text{ml aliquot of solution}} =$$

μg of uranium per cubic meter of air

NOTE: High readings for blanks may result from any of the following ten sources:

1. Dark current or zero drift in the fluorophotometer.
2. Fluorescence of fluorophotometer parts.
3. Light leakage in the fluorophotometer.
4. Fluorescence of dust particles or grease on dishes or disks after fusion.
5. Uranium introduced by touching dishes or fusion material.
6. Uranium introduced by splattering during evaporation.
7. Uranium introduced as dust from the atmosphere.
8. Uranium present in the original fusion material.
9. Uranium introduced from the platinum dishes.
10. "Blank rise" from standing in air (due to moisture absorption).

PREPARATION OF STANDARD CURVES

Three standard curves are prepared and read every month. In addition, new curves are made when dark current or zero drift is noted in the fluorophotometer, a new lamp is installed, a new lot of sodium fluoride used, or whenever there is a change in procedure or instrument behavior.

Each standard is done in triplicate and 2 blank dishes are prepared. These are treated as given under the procedure for samples beginning with Step 6.

Curve 1 - 0.01, 0.025, 0.05, 0.075, and 0.10 ml (10, 25, 50, 75 and 100 microliters) of Standard I are pipetted in triplicate onto the platinum dishes. This gives standards containing 10^{-7} , 2.5×10^{-7} , 5×10^{-7} , 7.5×10^{-7} , and 10^{-6} g of uranium per dish. This set of standards is read with sensitivity scale 1.

Curve 2 - 0.01, 0.025, 0.050, 0.075, and 0.10 ml of Standard II are pipetted in triplicate onto the platinum dishes. This gives standards containing 10^{-8} , 2.5×10^{-8} , 5.0×10^{-8} , 7.5×10^{-8} , and 10^{-7} g of uranium per dish. This set of standards is read with sensitivity scale 1.

Curve 3 - 0.01, 0.025, 0.050, 0.075, and 0.10 ml of Standard III are pipetted in triplicate onto the platinum dishes. This gives standards containing 10^{-9} , 2.5×10^{-9} , 5.0×10^{-9} , 7.5×10^{-9} , and 10^{-8} g of uranium per dish. This set of standards is read with sensitivity scale 2. (Sensitivity scale 3 is too sensitive for use.)

The fluorescence of the disks is read and the standard curves are plotted with grams of uranium per dish vs. the vernier readings for the standards minus the vernier reading for the blank.

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ELECTRODEPOSITION OF ENRICHED URANIUM IN URINE

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INTRODUCTION

The detection of uranium taken into the body through the respiratory and gastrointestinal systems is greatly facilitated by the determination of microquantities of uranium in the urine of individuals. The majority of methods currently in use consist of a tedious and time-consuming preparation. Then an extraction with an organic solvent is necessary before evaporating the material on a plate for counting. The sample load in the laboratory is such that it requires a rather quick and simple method without adversely affecting the unit cost of the analyses.

A modified version of the electrodeposition method reported by Cohen and Hull⁽¹⁾ is used in Y-12 for determining enriched uranium in urine. The major modifications - individual power supplies for each cell, more simple cell assembly, and circulation of the electrolyte by gas evolution from the electrodes in a slightly tilted sample holder - were made by Pflasterer and Zimmerman.⁽²⁾ The method consists of a simple digestion with nitric acid, and the electrodeposition of insoluble hydroxides or carbonates of uranium on silver disks at the cathode. The alpha emission is counted in Nuclear Measurements Corporation Model PC2 proportional counters.

COLLECTION AND PREPARATION

Approximately 580 individuals are scheduled to participate in the enriched urine analysis program. Of this number, 50 per cent participate each week and the remainder not less than once per month. Each participant is scheduled to void a sample on an assigned date which is always preceded by two scheduled off days. The sample is voided both prior to entering the work area and changing into clothing which have been worn in the work area. Such a procedure reduces the probability of sample contamination and the elimination of recently inhaled material. The participant is requested to enter the time of the present and previous voiding on the label; this enables the laboratory to calculate the time interval represented by the sample. The sample remains under refrigeration for a period of 2 to 20 hours before delivery to the laboratory. The samples are prepared for electroplating within 24 hours after receipt.

Upon receipt by the laboratory, the volume of urine is measured and the time interval of the sample is entered on a prepunched IBM card which has been previously prepared from a scheduled participation list. The sample is then ready for analysis.

REAGENTS AND APPARATUS

1. All chemicals should be reagent grade.
2. Nitric acid, concentrated.
3. Ammonium hydroxide. Approximately 8N.
4. Ferric ammonium oxalate solution. Dissolve 454.4 grams ammonium oxalate and 3.44 grams ferric ammonium sulfate in 16 liters of distilled water.

5. Steam bath.
6. Beckman automatic titrater.
7. Brewer automatic pipette machines.
8. Silver disks. 1-3/4" diameter, 0.002" thick. The disks must be thoroughly cleaned.
9. Electroplating cells. Figures 1, 2, and 3 show the size, power supply and arrangement of these cells. Coiled platinum electrodes, nickel-plated flat disk electrodes, chimneys with an etched ring at the 60-ml level, metal lids with hole in center for cathodes, and rubber gaskets are essential parts of these cells.
10. Glassine bags.
11. Nuclear Measurements Corporation Model PC2 proportional counters.
The low background chamber marketed by NMC is preferred.

PROCEDURE

The sample preparation is simple. It consists of digesting to dryness 20 ml of each urine sample with 15 ml of concentrated nitric acid on a steam bath. The salts are put in solution with approximately 10 ml distilled water.

To the prepared sample in a 150-ml beaker, add 20 ml of ferric ammonium oxalate solution and adjust the pH of this solution to 5.0 with ammonium hydroxide. Transfer the solution to the assembled chimney, make volume up to etched ring and fasten electrode connections. Turn on the power supply switch and set the rheostat to deliver 2.5 amperes until either the solution foams or reaches a

Figure 1

Figure 2

Figure 3

temperature of approximately 95°C. When either of these conditions occur, reduce the current to 1.5 amperes and keep at this point until plating time is complete. The total plating time is 50 minutes. The plated disk is removed, blotted dry with Kleenex, and placed in a properly marked glassine bag. Finally, the sample is counted for 30 minutes in each of three counters. A modified form of Chevanant's criterion is used to reject any individual count on statistical grounds. The short counting times are justified, since for a 90-minute count, the counting error is comparable to the analytical error.

Two samples of blank urine are analyzed each day as spot checks for contamination introduced within the procedure. These samples should not exceed 5×10^{-9} $\mu\text{c/ml}$. The efficiency of the analysis is routinely determined by analyzing samples containing a known amount of uranium. Two samples containing 1.43×10^{-7} $\mu\text{c/ml}$ are analyzed each day. These efficiencies average between 65 and 75 per cent.

The raw data from the analyses are then entered on the previously mentioned IBM cards and then submitted to the tabulating service group for final processing. The IBM equipment makes the necessary calculations from the data and automatically prepares the final report. This report includes all of the exposure data for each individual for the most recent 13-week period. Such a procedure enables responsible supervision in the evaluation of not only the present exposure but also the effect of samples previously submitted.

QUALITY CONTROL PROGRAM

Recently, a quality control program was inaugurated as a supplement to the internal control program. This program is administered by

a completely independent statistical control group. The control samples are introduced into the laboratory along with the routine samples and therefore are processed in the same manner. The results of the most recent 48 control samples indicate a Limit of Error at the 95 per cent confidence level of ± 74 per cent with a sample bias of 22 per cent ± 23 per cent. All of these 48 samples contained 1.79×10^{-6} μc of uranium in varying volumes. The reported mean for these samples was $2.32 \times 10^{-6} \pm 0.54 \times 10^{-6}$ μc . It is obvious that these levels of uranium concentrations require ideal environmental conditions for analysis.

DISCUSSION

Calcium will deposit on top of the uranium, reducing the counting efficiency, if large amounts are present in the urine sample. It has been found that such deposition does not occur appreciably during the first 50 minutes of plating; thus, the plating time becomes an important consideration. Gallimore and Royster⁽³⁾ are studying this effect by using a synthetic urine salt base as an electrolyte to achieve higher recoveries. They have obtained recoveries consistently in excess of 90 per cent from urine of low specific gravity.

The effect of self-absorption and absorption of other metals which may be present in urine has not been investigated. However, it is planned to study this with a recently acquired alpha range analyzer.

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DETERMINATION OF FLUORIDE IN WATER

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Many investigators have sought a simple, rapid, and accurate method for the determination of fluoride in water. The event of fluoridation of public water supplies has increased the interest in such a method. Also, greater use of fluoride compounds in industrial processes has focused further attention on the control of fluoride pollution of streams. The literature on methods for the determination of fluoride is rather abundant. The most troublesome problem is the effect of interfering substances. This is magnified when industrial wastes are analyzed.

Many complexing reagents and reactions have been used. Considerable work has been done in developing and modifying techniques to inhibit the interferences, but the complexing agents and reactions have not been sufficiently specific. In general, one technique or method will inhibit certain interferences and conversely magnify others.

The zirconium-alizarin procedure is simple, convenient, and accurate when substances which interfere are within tolerable limits. However, for the accurate determination of fluoride in many industrial wastes, the prior isolation of fluoride by distillation is necessary. Fluoride may be determined accurately on all or at least practically all water samples when a proper isolation technique is used, but this is time-consuming. The distillation of fluoride must be handled with a rather precise technique, to provide essentially complete recovery.

The tenth edition of "Standard Methods for the Examination of Water, Sewage, and Industrial Wastes"⁽¹⁾ provides a distillation procedure and three modifications of the zirconium-alizarin procedure, i.e., Megregian-Maier, Scott-Sanchis, and Lamar. Lamar and Drake published a more detailed study of the zirconium-alizarin procedure in the June, 1955, issue of the Journal of the American Water Works Association.⁽²⁾ The Tentative Methods of Test for Fluoride Ion in Industrial Water and Industrial Waste Water,⁽³⁾ adopted by the American Society for Testing Materials, consist of a referee method using prior isolation of the fluoride by distillation and a non-referee method using a direct zirconium-alizarin procedure. These methods are essentially as prescribed by Lamar and Drake. Grutsch and co-workers⁽⁴⁾ used the addition of thioglycolic acid in the zirconium-alizarin method to eliminate some interferences. It is claimed that this reagent eliminated the interference of iron, manganese, and residual chlorine. However, when the zirconium-alizarin indicator is acidified with sulfuric acid, the interference of iron and manganese is usually negligible in potable waters. In alkaline waters, appreciable iron usually precipitates readily and may thus be removed.

Saylor and Larkin⁽⁵⁾ reported on the titration of fluoride with aluminum chloride, using eriochrome cyanine R as an internal indicator. In 1954, Megregian⁽⁶⁾ reported on the spectrophotometric determination of fluoride with zirconium-eriochrome cyanine R. Since sulfate interfered critically, a nomograph was provided for the correction of this interference. However, this method is not as subject to the other

interferences studied as the zirconium-alizarin. A modified procedure with zirconium and eriochrome cyanine R is presented in this paper. In this modification, sulfate interference is eliminated by removal of the sulfate by precipitation. This paper will be devoted to a presentation and comparison of the zirconium-alizarin and zirconium-eriochrome cyanine methods. A distillation technique which has given good recovery is also provided.

ZIRCONIUM-ALIZARIN METHOD

The determination of fluoride with the zirconium-alizarin reagent is based on the ability of the fluoride ion to form the zirconium fluoride complex, ZrF_6^{--} . This results in proportionate subtraction of zirconium from the zirconium-alizarin indicator. It varies, when fluoride is present, in color intensity, ranging from pink to yellow-green, with intermediate combinations in quantitative proportion to the concentration of the fluoride ion. As the color approaches yellow-green, the test is less sensitive.

Zirconium-alizarin is used rather extensively for the determination of fluoride in water, which is done readily by the addition of a single reagent. This method, as well as others, is subject to interferences from various substances. Small to large errors may ensue, depending upon the effect of one or more of the interferences. Reaction timing and temperature differentials are critical for readings made at 1 hr, but are not significant when the reaction time is sufficient to approach equilibrium conditions (over 7 hr). Temperature differentials are automatically adjusted for readings taken at over 7 hr.

Reagents and Preparation

All reagents should conform to specification of the Committee on Analytical Reagents of the American Chemical Society.⁽⁷⁾ When the specifications are not known, the chemicals used must be sufficiently pure to obtain the required accuracy. The acid indicator and alizarin should be stored in the dark, the fluoride standard being kept in resistant glass or polyethylene.

Zirconyl Nitrate or Zirconyl Chloride. Dissolve 1.84 g $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ or 2.22 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 250 ml distilled water. If a turbid solution results, it should not be filtered because this turbidity may be due to some insolubility of the zirconyl salt rather than to impurities. However, if the turbidity persists after mixing with the alizarin and sulfuric acid, the reagent should be discarded.

Alizarin Red S (Certified). Dissolve 0.37 g alizarin monosodium sulfonate in 250 ml distilled water.

Sulfuric Acid, 2.1N.

Acid Indicator. Add 25 ml of the zirconyl solution to 50-100 ml distilled water. With constant stirring, slowly add 25 ml of the alizarin solution. Make up to 500 ml with distilled water. Mix well and add 500 ml of 2.1N sulfuric acid. The acid indicator, which is ready for use in about 1 hr, should be clear. This reagent is quite stable, particularly when stored in the dark, so that refrigeration is not necessary. If a precipitate forms or a poor color range develops, a fresh reagent should be prepared.

Sodium Arsenite (Metal). Dissolve 0.916 g NaAsO_2 in distilled water and dilute to 500 ml.

Sodium Fluoride. Stock solution: dry at 150°C and dissolve 0.2210 g sodium fluoride in fluoride-free distilled water and make up to 1 liter. Standard solution: dilute 100 ml stock solution to 1 liter with fluoride-free distilled water, so that 1 ml contains 0.01 mg fluoride.

Fluoride-free distilled water.

Procedure

Transfer 100 ml, or a volume containing not more than 0.14 mg fluoride, of the clear samples to Nessler tubes. If the volume of the sample taken is less, make up to the full quantity with fluoride-free distilled water. Although concentration of the fluoride ion as high as 0.14 mg can be compared, the accuracy is improved if the amount of fluoride is limited to not more than 0.10 mg. The most sensitive range is from about 0.03 to 0.07 mg fluoride. Matched Nessler tubes, preferably the short form, should be used throughout the procedure. If chlorine is present, it should be removed by adding a slight excess of the sodium arsenite solution. Use 0.1 ml for each 0.1 mg chlorine in the sample aliquot, plus 0.1 ml excess.

Prepare a series of standards in intervals of 0.01 mg fluoride, covering the anticipated range of the samples. Make the standards up to 100 ml with fluoride-free distilled water. To each of the samples and standards, add exactly 10 ml of the zirconium-alizarin reagent and mix well. Matched Nessler tubes should be used so that the height of the liquid in samples and standards is the same, or practically so. Compare the samples to the standards in a three-hole comparator

(see Fig. 1) using diffused daylight or a fluorescent daylight lamp.

The readings may be made at the end of a 60-minute reaction time if the reagent was added to all the tubes within 2 minutes, provided both test elements are maintained at the same temperature. The time allowance is made on the basis of a maximum permissible difference in color comparison equivalent to 0.005 mg fluoride. If the results are not needed promptly, the most satisfactory procedure is to make the comparisons after a reaction time of 7-18 hr, when color range is better. Moreover, the temperature and the time used in adding the reagent are not critical. When the reaction time is 7 hr or more, differences up to 1 hr in the ages of the samples and standards are permissible. Inspection of the samples will indicate any concentration of fluoride requiring a smaller aliquot, which may be taken and prepared within the 1-hr limit.

Interferences

Some of the ions commonly found in natural and treated waters affect the reaction in such a manner that the fluoride concentration appears to be higher than its true value, other ions having the opposite effect. The individual interference of appreciable quantities of calcium (200 ppm), magnesium (200 ppm), sodium (1,000 ppm), potassium (200 ppm), and nitrate (600 ppm) is negligible. However, in concentrated samples, noticeable interference from some substances may generally be expected to the extent that isolation of the fluoride by distillation is advisable. The effect of other substances investigated is shown in Table I.

Fig. 1. Three-Hole Comparator

TABLE I. EFFECT OF INTERFERING SUBSTANCES

SUBSTANCE	IN SAMPLE ALIQUOT (mg)	WITH 100-ML ALIQUOT (ppm)	FLUORIDE ERROR WITH 100-ML ALIQUOT (ppm)
Al ⁺⁺⁺	0.02	0.2	-0.05
Fe ⁺⁺	1.5	15	-0.02
Fe ⁺⁺⁺	1.5	15	-0.02
Mn ⁺⁺	2.5	25	0.00
Cr ⁶⁺	0.05	0.5	+0.05 ^a
SO ⁻⁻	40	400	+0.06
Cl ⁻	50	500	-0.06
NO ₃ ⁻	60	600	-0.05
PO ₄ ⁻⁻⁻	0.2	2.0	0.04 ^b
Alkalinity as CaCO ₃	12.5	125	-0.06
pH scale	2.8	--	+0.06

a. Maximum for 1-hr readings; decreases with fluoride concentration.

b. Maximum for 7 to 18-hr readings. The error varies with the concentration of fluoride and phosphate and is mostly negative except for some combinations, such as 0.10 mg fluoride and 0.01 mg phosphate when it is positive.

When the summation of the interferences does not exceed the equivalent of 0.1 ppm fluoride, no corrections are necessary, as this is about the accuracy of routine analysis without prior isolation of the fluoride by distillation. Although good results can be obtained by the

application of limited corrections, isolation of the fluoride will provide the maximum accuracy, particularly when the total interference exceeds the equivalent of 0.1 ppm fluoride. Moreover, when the composition of the water is not known, distillation is required.

The aluminum ion causes a negative error, because of the formation of an aluminum-fluoride complex which limits the availability of the fluoride ion for formation of the ZrF_6^{--} ion. The magnitude of the difficulty is dependent on the amount of aluminum and fluoride present. The percentage of the fluoride complexed by the aluminum was found to be constant, for a given concentration of the latter, within the limits of experimental error.

It is possible to correct the fluoride reading for interference due to aluminum. A plot (see Fig. 2) of the ratio of true to apparent fluoride against aluminum provides a convenient means for obtaining the correction factor. For concentrations of aluminum in the sample aliquot, the true fluoride is obtained by multiplying the apparent fluoride by the ratio or factor taken from Figure 2. This factor is valid for reaction times of 1 hr and 7-18 hr. Corrections for other interfering substances must be made prior to the correction for aluminum.

Very small amounts of aluminum have a varying effect on the fluoride measurement, depending upon the concentration of fluoride. The presence of 0.02 mg aluminum in the sample aliquot causes a negative error equivalent to 0.005 mg fluoride. For higher aluminum concentrations, the error varies according to the fluoride concentration in the

Fig. 2. Ratio of True to Apparent Fluoride

sample aliquot. For fluoride concentrations not exceeding 0.10 mg and aluminum concentrations not exceeding 0.05 mg, the maximum of the variable errors will not exceed the equivalent of ± 0.01 mg fluoride.

The presence of hexavalent chromium causes a positive error in the fluoride determination. This effect varies inversely with the concentration of fluoride and directly with the concentration of chromium and the reaction time. The maximum fluoride error caused by hexavalent chromium is as follows: For 1-hr readings, the fluoride error will not exceed $+0.005$ mg F when the hexavalent chromium in the sample aliquot does not exceed 0.05 mg. For 7 to 18-hr readings, the fluoride error will also not exceed $+0.005$ mg F when the hexavalent chromium does not exceed 0.01 mg. When the chromium in the sample aliquot exceeds 0.01 mg, the fluoride readings should be taken at 1 hr; when it exceeds 0.05 mg, the fluoride should be isolated by distillation.

Ferrous or ferric iron up to 1.5 mg in the sample do not cause any significant amount of interference, but 2.5 mg of iron does interfere, as the zirconium-alizarin lake and free alizarin colors are obscured. Manganese does not produce any significant interferences in quantities as high as 2.5 mg in the sample aliquot.

The presence of sulfate increases the fluoride reading, while chloride and alkalinity decrease it. These effects are substantially additive, and corrections may be applied up to 100 mg sulfate, 200 mg chloride, and 50 mg alkalinity as CaCO_3 in the sample aliquot (see Fig. 3). There is no difference in the effect of bicarbonate, carbonate, and hydroxide alkalinity. When a sample of less than 100 ml is taken, the alkalinity of the diluted sample must be used.

Fig. 3. Correction Curves for Sulfate, Chloride, and Alkalinity

The interference of nitrate is negative, but it is negligible for quantities found in natural and potable waters. This interference is only equivalent to -0.002 mg F for concentrations of nitrate (NO_3) up to 30 mg in the sample aliquot.

Phosphates as PO_4 or as $(\text{NaPO}_3)_6$ are similar in their effects, decreasing or increasing the fluoride reading according to the quantities of phosphate and fluoride present, and varying with the reaction time. It is possible that there may be simultaneous complexing of fluoride with phosphate, decreasing the apparent fluoride, and formation of secondary zirconium phosphate, increasing the apparent fluoride. If these reactions proceed at different rates they may be the cause of the variable interference.

When the concentration of fluoride in the sample aliquot is not more than 0.10 mg, the maximum of the variable interferences of phosphate as PO_4 is as follows: (1) for 1-hr readings when the phosphate does not exceed 0.10 mg, the error is not more than 0.004 mg fluoride; (2) for 1-hr readings when the phosphate does not exceed 0.20 mg, the error is not more than 0.007 mg fluoride; and (3) for 7-18 hr readings when the phosphate does not exceed 0.20 mg, the error is not more than 0.004 mg fluoride. If the concentration of phosphate in the sample aliquot exceeds these limits, the fluoride should be isolated by distillation. For the ranges of fluoride and phosphate given, the errors are mostly negative. For several combinations of the higher concentrations of fluoride and the lower concentrations of phosphate, however, the error is positive, the maximum positive occurring for the combination of 0.10 mg fluoride and 0.01 mg phosphate.

Acidity increases the fluoride indication below pH 4.5, but at pH 3.5 the effect is only +0.002 mg F and at pH 3.0 it is +0.004 mg F.

The comparison of the samples is obscured by turbidity and color of the water. Turbid samples should be filtered clear. The effect of color may be compensated for to a limited extent. Place the sample above a Nessler tube containing distilled water; place the standard above a duplicate sample which has been acidified with 5 ml of 2.1N sulfuric acid. Each tube should be made up to contain equal volumes.

ZIRCONIUM-ERIOCHROME CYANINE METHOD

The determination of fluoride with zirconium and eriochrome cyanine is also based on the ability of the fluoride ion to form zirconium fluoride complex, ZrF_6^{--} . The formation of this complex restrains a proportionate amount of zirconium from the indicator and the color change can be measured photometrically. In strong acid solution, the indicator used in this procedure ranges in color from red to orange.

This procedure is less subject to interference than the zirconium-alizarin method. Of the ions studied, the interference of sulfate concentrations present in water was the most critical. This interference varies with both the concentration of fluoride and sulfate. In the original procedure by Megregian, a nomograph was given for the correction of the sulfate interference. The modification given in this paper was developed by J. H. Hubble of our Columbus laboratory. In this procedure, the sulfate interference is eliminated as prescribed by L. I. Thatcher of our Washington laboratory.

Reagents and Preparation

Reagent Specifications. See Zirconium-Alizarin method.

Eriochrome Cyanine R Solution. Dissolve 1.800 g of eriochrome cyanine R in 1 liter distilled water. This organic chemical is designated as (National) Color Index No. 722.

Zirconyl Solution. Dissolve 0.220 g $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ or 0.265 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, in about 100 ml of distilled water, add 700 ml of concentrated HCl (sp gr 1.19) and dilute to 1 liter.

Hydrochloric Acid Solution. Dilute 700 ml concentrated HCl (sp gr 1.19) to 1 liter with distilled water.

Barium Chloride Solution. Saturate about 1 liter of distilled water with $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

Sodium Arsenite (Meta). See Zirconium-Alizarin method.

Sodium Fluoride Solution. See Zirconium-Alizarin method.

Fluoride-free distilled water.

Procedure

Use a 50-ml aliquot or less, containing not more than 0.07 mg fluoride. If the volume of the aliquot is less than 50 ml, dilute to 50 ml with fluoride-free distilled water. Add exactly 5 ml of eriochrome cyanine R solution, stir, and add exactly 5 ml of the zirconium-hydrochloric acid solution. Stir, and let stand for about 3 minutes. Add 2 ml of the saturated barium chloride solution and stir. Allow the sample to stand about 3 hours or until the precipitate has completely settled or the sample may be centrifuged. (Filtration by paper is not satisfactory.) Prepare a reference solution with dis-

tilled water in the same manner except that 5.0 ml of the hydrochloric acid solution is added, instead of the zirconium-hydrochloric acid reagent.

Fill a cell with the sample and another cell with the reference solution. The sample must not contain any of the barium sulfate. Adjust the temperature of the sample and reference solution to within 3°C of the temperature of the standard curve.

The spectrophotometer is set at zero absorbancy with the reference solution at the appropriate wave length, about 535 mu, depending upon the instrument and eriochrome-cyanine dye used. Determine the fluoride concentration from a standard curve prepared by the above procedure, using the standard sodium fluoride. A new standard curve must be made whenever new solutions are prepared. The standard curve must also be checked at several points within the applicable concentration range whenever the fluoride is determined.

When water samples contain color or turbidity, a correction procedure is necessary as follows: take a duplicate aliquot of the sample and proceed as with the reference solution. This duplicate is read against the reference solution in the same manner as the original sample. Subtract algebraically the absorbance of the duplicate sample from the absorbancy of the original sample. The fluoride concentration is determined from the net absorbancy.

The interference of aluminum up to 0.25 mg in the sample aliquot is eliminated by the 3-hour standing necessary for the settling of the barium sulfate precipitate. If centrifuging is used instead of settling, it is necessary to wait 2 hours when aluminum is present.

Chlorine must be removed or reduced before adding any of the reagents. If chromium and manganese are absent, the chlorine may be reduced by adding a slight excess of the sodium arsenite solution. Use 0.1 ml for each 0.1 mg of chlorine present in the sample aliquot plus 0.1 ml excess. When chromium or manganese are present, interference develops with the use of sodium arsenite. About 30 minutes of vigorous stirring with a mechanical stirrer will generally remove the chlorine sufficiently when sodium arsenite cannot be used for this purpose.

Interferences

In the Megregian procedure, sulfate produced considerable interference and a nomograph was provided for the correction. This interference varied with the concentration of both sulfate and fluoride. The modification given in this paper eliminates the interference of sulfate by removal through precipitation.

Sodium arsenite may be used to eliminate the interference of chlorine when manganese and chromium are absent. However, when present, sodium arsenite causes either of these constituents to interfere.

Table II gives the tolerances reported by Megregian. It should be understood that the tolerances reported in this table specifically refer to the Megregian procedure published in July, 1954, issue of Analytical Chemistry.

TABLE II TOLERANCES REPORTED BY MEGREGIAN

SUBSTANCE	CONCENTRATIONS WHICH PRODUCE 0.02 PPM FLUORIDE ERROR	
	In Sample Aliquot (mg)	With 50-ml Aliquot (ppm)
Al ⁺⁺⁺	0.25 ^a	5.0 ^a
Fe ⁺⁺⁺	0.50	10.0
Cl ⁻	175	3,500
PO ₄ ⁻⁻⁻	0.125	2.5
(NaPO ₃) ₆	0.050	1.0
Alkalinity as CaCO ₃	165	3,300

a. When reaction is permitted to continue for 2 hr

TABLE III TOLERANCES OF VARIOUS SUBSTANCES
TO THE EXTENT INVESTIGATED

Substance	In Sample Aliquot (mg)	With 50-ml Aliquot (ppm)	Substance	In Sample Aliquot (mg)	With 50-ml Aliquot (ppm)
SiO ₂	2.5	50	Na ⁺	100	2,000
Al ⁺⁺⁺	0.25 ^a	5 ^a	Li ⁺	0.25	5
Fe ⁺⁺⁺	0.5	10	HCO ₃ ⁻	100	2,000
Mn ⁺⁺	0.25	5	SO ₄ ⁻⁻	Remove	Remove
Cr ⁶⁺	0.25	5	Cl ⁻	150	3,000
Cu ⁺⁺	0.15	3	NO ₃ ⁻	25	500
Pb ⁺⁺	0.15	3	PO ₄ ⁻⁻⁻	0.25	5
Zn ⁺⁺	0.15	3	Phenol	0.25	5
Ca ⁺⁺	25	500	Dissolved Solids	250	5,000
Mg ⁺⁺	10	200	Color & Turbidity	Compensate	Compensate

a. When reaction is permitted to continue for 2 hr

A study was made of the effect of interferences in the modification described in this paper. In this study, the chemical referred to as eriochrome cyanine R, Color Index No. 722 was a product of National Aniline Division of the Allied Chemical and Dye Corporation and was called Alizarol Cyanone RC. Table III shows the concentration of various substances which did not interfere. These concentrations do not necessarily represent the maximums which may be tolerated but instead represent the maximums investigated which did not interfere in the modified procedure given in this paper.

The data in Table III was derived from a study of each of the individual substances and from various combinations of them. In another modification, Thatcher reported that 10 ppm of phosphate showed a slight positive effect in standards containing no fluoride but showed no interference at the 1 ppm level. He also reported that iron, manganese, copper, lead, and zinc showed no significant interference at 5 ppm.

ISOLATION OF FLUORIDE

When interfering substances are present in significant quantities, it is necessary to provide for their removal prior to the fluoride determination. This may be accomplished by a suitable distillation of the sample, a procedure described in following paragraphs. The fluoride is distilled as hydrofluosilicic acid. Preliminary concentration of the sample is necessary to promote complete recovery.

Apparatus

The device shown in Figure 4 consists of a steam-generating assembly, a fluoride distillation section, and a distillate-receiving flask. Rubber

Fig. 4. Distillation Assembly for Fluoride Isolation

connections are used on the steam-generating assembly, while ground glass joints are used on the fluoride distillation section. This was modified from a commercial fluoride distillation apparatus. The hot-water reservoir (B) supplies boiling water to the steam generator (E). The pressure control tube (A) serves as a steam release. When boiling water is needed in the steam generator (E), the clamp (D) is released and air pressure is applied to the tube (A). Before each use, the distillation section is washed thoroughly, followed by thorough rinsing with distilled water.

Figure 4. Distillation Assembly for Fluoride Isolation

- A. Pressure control tube.
- B. Hot-water reservoir, 1,000 ml.
- C. Hot plate.
- D. Hot-water supply tube clamp.
- E. Steam generator flask, 1,000 ml.
- F. Heating mantle.
- G. Pressure relief tube.
- H. Steam regulation tube, with Hoffman clamp.
- I. Glass steam line (asbestos covered).
- J. Steam trap (asbestos covered), with clamp on relief water drain.
- K. Steam inlet tube, with Hoffman clamp.
- L. Fluoride distillation flask adapter.
- M. Fluoride distillation flask, 300-ml.
- N. Heating mantle with asbestos shield.
- O. Thermometer, 250°C.
- P. Trap
- Q. Condenser adapter.
- R. Condenser.
- S. Distillate-receiving flask, 200-ml.

Reagents

These are: (1) sodium hydroxide pellets; (2) sulfuric acid, concentrated; (3) silver sulfate powder; and (4) phenolphthalein indicator.

Distillation Procedure

Transfer 200 ml of the sample to the fluoride distillation flask, make alkaline to phenolphthalein with a pellet of sodium hydroxide, add

some glass beads, and evaporate to a volume of 15-20 ml, preferably using an electric heating mantle. Care must be exercised to prevent bumping, which will result in loss of sample. Allow the concentrated sample to cool and add sufficient silver sulfate (a slight excess will do no harm) to precipitate any chloride. Connect the distillation assembly, except for the steam inlet tube (K). In place of this, insert a long-stemmed cylindrical separatory funnel. Start a flow of cooling water through the condenser, close the stopcock of the funnel and introduce 20 ml of concentrated sulfuric acid into it (Note 1). Slowly add the acid to the fluoride distillation flask, regulating the flow of acid by means of a stopcock. Remove the funnel (wash the tip of the funnel into the flask). In its place, insert the steam inlet tube, connecting it to the steam trap (J). Start the flow of steam through the sample by opening the clamp on the steam inlet tube (K) and by closing the clamp on the steam regulation tube (H). Adjust the clamp so that a hydrostatic head of 20-40 cm is maintained in the steam generator pressure relief tube (G). The distilled water in the steam generator should be made slightly alkaline to phenolphthalein with NaOH.

Apply heat to the distillation flask with the heating mantle (N). Use a shield of asbestos at the top of the mantle to prevent undue heating of the flask walls. Heat should never be applied above the surface of the liquid. Collect enough distillate to fill a 200-ml volumetric

Note 1. An excess of sulfuric acid must be maintained during the distillation. If the sample is extremely alkaline, add 20 ml of sulfuric acid in addition to that required to neutralize the sample.

flask while maintaining the temperature of the sample at 135-145°C, accomplished by the adjustment of the steam flow and the amount of heat applied. The distillate will be free of interfering substances so that the fluoride may be determined by either of the methods as previously described.

COMPARISON OF METHODS

Several modifications of the zirconium-alizarin method, including the visual and photometric, are widely used for the determination of fluoride in water. The U. S. Geological Survey has used the zirconium-alizarin procedure for the determination of fluoride in many thousands of water samples from various sources throughout the United States. When the other substances in the water are within tolerable limits, this method is simple, convenient, and accurate. Corrections for interfering ions may be applied within limits. When isolation of the fluoride is necessary, this procedure may be used to provide accurate results. The principal disadvantage of the zirconium-alizarin method is the extent to which it is subject to interferences.

The zirconium-eriochrome cyanine method is generally less subject to interferences. In the original method, the interference of sulfate was the most critical. This interference can be eliminated by the removal of sulfate by precipitation. Organic reagents from different manufacturers may show differences in chemical and physical properties. The eriochrome cyanine R from two manufacturers was examined by our Washington laboratory. One product was dark brown in color and the other was reddish-tan. The absorbancy curves for these two products

were quite different. Also, the eriochrome cyanine R chemical appears on the market under different designations. The product we used was called Alizarol Cyanone RC by the manufacturer and was listed by the distributor as Alizarine Cyanone RC.

Since the zirconium-eriochrome cyanine method is less subject to interference, it bears promise of being generally more satisfactory than the zirconium-alizarin procedure. However, there has been considerable study and experience with the zirconium-alizarin method while more study and experience with the zirconium-eriochrome cyanine method is needed.

The U. S. Geological Survey has made some comparative studies of the zirconium-alizarin and zirconium-eriochrome cyanine methods, in which 14 of our laboratories participated. Four standard ampoules containing 0.23 to 1.22 ppm sodium fluoride, one of which also contained 5 ppm sodium phosphate, were supplied to each laboratory. The concentrations present were not known by any of the laboratories when the tests were made and reported. In this study, a prescribed modification of the zirconium-eriochrome method was used while each laboratory employed the zirconium-alizarin procedure which was in regular use at that laboratory. In general, this was the zirconium-alizarin modification described in this paper. In reporting, some of the laboratories rounded-off their results to the nearest tenth ppm fluoride.

A compilation and study of the data provided the following information: A total of 56 tests were made by the 14 laboratories by the zirconium-alizarin procedure and the same number by zirconium-eriochrome cyanine procedure. The maximum lack of agreement for each of the two procedures was on the ampoule containing the most fluoride (1.22 ppm).

The zirconium-alizarin procedure provided a recovery within 0.1 ppm fluoride, except for 2 results where the difference was -0.2 and +0.3 ppm fluoride. One of these differences, -0.2 ppm fluoride, was on the ampoule containing 5 ppm sodium phosphate for which no correction was applied.

The zirconium-eriochrome cyanine procedure provided a recovery within 0.1 ppm fluoride, except with 4 results where the differences ranged from -0.2 to +0.4 ppm fluoride.

The four standard ampoules were also determined at the Columbus laboratory by the modified zirconium-eriochrome cyanine procedure reported in this paper. The samples were centrifuged and the readings were taken at approximately 4 hours. The results agreed within +0.01 and -0.03 ppm of the fluoride reported to be present. When the reaction was allowed to continue overnight (about 22 hr), the results agreed within -0.03 and +0.04 ppm fluoride.

Recovery tests were made by our Washington laboratory on 10 water samples having a range in dissolved solids from 93 to 2,620 ppm. The fluoride content was initially determined by the zirconium-eriochrome cyanine method. Exactly 1 ppm fluoride was added and the fluoride was redetermined by the same method. The results show that from 92 to 105 per cent of the fluoride added was recovered.

A comparative study of the fluoride content of over 200 water samples from various sources was made by the Columbus laboratory by the two methods described in this paper without isolation by distillation. The results by these two methods were generally in agreement within 0.1 ppm fluoride.

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DETERMINATION OF TRITIUM IN URINE AND WATER⁽¹⁾

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The necessity for determining tritium at low levels for purposes of health protection has led to the development of methods for the detection of tritium in the atmosphere and of methods for the quantitative determination in aqueous solutions such as biological fluids and water. It is our purpose here to describe the method used to measure tritium at concentrations as low as one microcurie per liter of aqueous solution; on a gravimetric basis, this corresponds to 10^{-10} gram per liter.

Tritium in the elementary state (tritiated hydrogen) has been demonstrated by workers at Los Alamos to be a negligible hazard compared to tritium oxide (tritiated water), since the element is not absorbed by the body to an appreciable degree. The oxide, however, constitutes a genuine hazard, since it is rapidly taken into the body either through the lungs, through the gastro-intestinal tract, or even through the skin. Indeed, the tritium water taken into the body by any means is uniformly distributed throughout the body water in about one hundred and eighty minutes.

The analysis of tritium based upon its radioactivity is complicated by the fact that the beta radiation from tritium is profoundly weak. For this reason, it is impractical to measure tritium except when the material itself is used as an internal gaseous filling in suitable chambers or tubes. If tritium oxide be converted to the element, the

resultant tritiated hydrogen gas can be loaded into suitable containers in which it may be measured by the ion current produced on an electrometer, or simply by counting the individual disintegrations on a suitable scaling device. Counting furnishes a useful answer much more rapidly and for this reason we have turned to the method of analysis described here.

Slide 1 (Note 1) shows the apparatus for filling counting tubes.

The apparatus depicted here serves to convert tritium oxide in aqueous samples to tritiated hydrogen. In the detachable generator at the left, the liquid sample is dropped onto metallic calcium; the tritiated hydrogen evolved is allowed to flow in the previously evacuated and sealed-off system through the drying tower and into the counting tube at the right. Calcium was selected as the reducing agent because the reaction is vigorous enough to minimize the possibility of fractionation even at room temperature. Gas is allowed to flow into the counting tube until a pressure of 15 cm of mercury is attained; then ethylene (2 cm Hg) and argon (5 cm Hg) are added to raise the total pressure to 22 cm of mercury. Ethylene is added as an internal quenching agent, while the argon is the ionizing gas. The tube is now ready for counting. The accessory valves and gauges attached to the system are used to govern the pressure at each stage of filling and mixing.

Slide 2 is a schematic representation of the counting tube.

The counting tube represented schematically here is of the external cathode type originated by Maze. It comprises a soft-glass

Note 1. Slides are not available for inclusion in this section of the report.

envelope, a tungsten center wire, and an external silver mirror cathode. A stainless steel spring serves to keep the center wire taut, while the silver mirror cathode is protected from mechanical damage by a wrapping of tape. The external cathode makes it possible to decontaminate the tube when necessary by flushing with strong mineral acid.

Slide 3 shows the shielding arrangement for counting.

The shield shown here in which the actual counting is done provides for the simultaneous counting of the sample tube and a tube similarly filled with inert hydrogen so that a fluctuating environmental background may be assessed and corrected for. Counting is carried out with Los Alamos Model 700 scalers at a potential 50 volts above the threshold voltage, customarily at about 1500 volts. Each tube is calibrated by filling with hydrogen generated from a standard tritium solution and counting. Using the procedure and pressures indicated, the filling from a water sample containing one microcurie of tritium per liter will cause a tube to count at about forty counts per minute over our usual background of 300 counts per minute. A trained operator can handle as many as 100 samples per day with a precision of ± 5 per cent.

Slide 4 shows small generation apparatus.

The need for more compact portable equipment of lower sensitivity has led to the development of a simpler apparatus whereby the tritiated hydrogen is led into ionization chambers of different sizes. The system is evacuated merely by water aspiration, doing away with the cumbersome vacuum pump. Measurement of the ion current produced may be

carried out on a vibrating reed electrometer (down to about 10 μc per liter) or on a Los Alamos ionization chamber current meter (down to about 250 μc per liter). The advantages of such smaller, less expensive equipment are apparent.

Slide 5 shows the I. C. C. M.

During the past several years, we have carried out more than 7,000 analyses on the urines of individuals suspected of exposure to tritium oxide. We have recorded a few of these to show what may be expected in such cases where personnel are exposed to atmospheres containing tritium oxide.

Slide 6 is a record of the urinary excretion of tritium of an individual who was exposed. The urinary concentration in microcuries per liter is represented on the vertical axis -- time, in days, on the horizontal axis. The initial value, 450 μc per liter, was picked up during routine daily sample analysis from an individual who had never before excreted tritium. The slope of the line indicates that tritium was being excreted with a biological half-time of 9 days. Tritium (as its oxide) is excreted after establishment of equilibrium within the body at a rate proportional to the tritium content of the body (assuming a constant water throughput) and excretion takes place in much the same way that radioactive materials decay. We are thus justified in speaking of a biological half-time, the time interval for half of the tritium remaining to be excreted. It is also possible from these data to calculate the body burden or the amount of tritium in the body immediately after exposure. This amount may be estimated by integrating under the

curve. This represents the total tritium excreted in the urine; a correction for the fraction of total water excreted by other channels gives a value of 19 mc for the body burden. Alternatively, the body burden may be calculated from the initial value alone; factors are applied for the water content of the body and the weight of the individual. This invariably yields values very close to those calculated by the previous method.

Slide 7 illustrates the highest exposure we have yet detected. This individual started off with an initial value of 2000pc per liter, indicating a body burden of some 69 mc. It has probably occurred to some that the excretion of tritium may be hastened simply by increasing the liquid throughput and in this case the biological half-time was cut down to eight days by the simple expedient of encouraging the individual to drink more water, coffee, beer, and the like.

Slide 8 illustrates an interesting case, a dermal exposure to anhydrous tritium bromide. The principal point of interest here is the not-unexpected fact that tritium absorbed in this form is excreted exactly as is tritium absorbed as water.

Slide 9 indicates roughly what may be expected of an individual who is exposed to frequent tritium doses of varying intensity during the course of his routine work. During the latter portion of the period represented here, the result of more effective control of tritium pollution of the air is apparent.

ABSTRACT

The sample is prepared for counting in a vacuum line. Urine or

water is dropped onto metallic calcium, and hydrogen and tritium are evolved. The gas flowing into the evacuated system is passed through liquid-nitrogen-cooled traps to remove unreacted water and condensable gases. The gas is allowed to flow into a tube similar to a Geiger-Muller tube until a pressure of 15 cm of mercury is attained. Ethylene and argon are added, to give a total pressure of 22 cm of mercury. The beta activity is counted with a scaling circuit having an input sensitivity of 1/4 volt. A tube similarly filled with inert hydrogen is counted simultaneously to determine the environmental background. The background count is subtracted from the sample count to obtain the true sample count.

The method has an efficiency of approximately 40 per cent and a precision of ± 5 per cent between the range of 1 to 150 $\mu\text{C}/\text{liter}$ of tritium. Samples with higher concentrations may be determined with appropriate dilutions. The tolerance for tritium in urine used at LASL is 250 $\mu\text{C}/\text{liter}$. The biological half-life of tritium is about 10 days. This may be decreased by increasing the fluid intake of the individual.

REAGENTS

Metallic Calcium - #10 mesh. The calcium used is a specially purified calcium obtained from R. D. Baker and associates at LASL (CMR-8).

Ethylene - 99.5%, Commercial grade

Argon - Commercial grade

Liquid Nitrogen

Apiezon N Stopcock Grease

The scaler has a 6-place mechanical register which will handle 72,000 counts per minute with a counting loss of less than 1 per cent. Two scalers are used -- one to count the background GM tube and one to count the sample GM tube. The scalers are equipped with a control panel and a Graylab Universal Timer so that they can be operated simultaneously for a preset time.

1. Turn on the master switch on both scalers and let the instruments warm for 30 minutes.
2. Turn on the AC switch on the control panel.
3. Fill the background GM tube with inert hydrogen (generated from distilled water) as described under the procedure for analyzing urine and water.
4. Turn on the high voltage on both scalers and let warm for 5 minutes. Turn off the high voltage. The high voltage must always be turned off when inserting or removing tubes in the lead pig in order to avoid shock.
5. Place the background GM tube in the lead pig with the anode (center wire) in contact with the high-voltage lead from the background scaler. Clip the ground lead from the background scaler to the copper foil cathode (the silver tube lining).
6. The scale selector switch on the scalers should be set for 100X.

II. Generating Sample

1. Fill the thistle tube on the generator with the urine sample (or water). This requires from 10 to 15 ml of liquid. Samples may be run on 5 ml if extreme care is used.
2. Close stopcock 3 to the vacuum pump.
3. Slowly drop the urine on the calcium until a mercury pressure of 16 to 17 cm of mercury is attained. (See the section on calibrating the manometer.)
4. Close stopcock 2 to close the left side of the manifold and open stopcock 1 to bleed the excess gas to the atmosphere.
5. With stopcock 3 (this stopcock is ground for micro-control), bleed off the gas in excess of 15 cm of mercury pressure.
6. The tube is now filled with hydrogen-tritium gas at a pressure of 15 cm of mercury. Close stopcock b on the tube.
7. Open stopcock 3 to the vacuum pump and evacuate the right side of the manifold to a pressure of 0.05 mm of mercury. Check with the Pirani gauge.
8. Close stopcock 4. (Leave stopcock 3 open.)
9. Using needle-valve c (to the ethylene cylinder), let ethylene flow into the system to such a pressure that opening stopcock b will give a final pressure of 17 cm

of mercury. Ethylene is added to the tube filling as a quenching agent.

10. Open stopcock b on the tube momentarily; the pressure of the entire system and the tube will fall to 17 cm of mercury.
11. Open stopcock 4 and evacuate the right side of the manifold.
12. When the manifold is evacuated, close valve 4 and, using needle valve d (to the argon cylinder), let argon flow into the system to such pressure that opening stopcock b will give a final pressure of 22 cm of mercury in the tube. Argon increases the specific ionization and lowers the starting potential of the counting tube.
13. Open stopcock b on the tube momentarily; the pressure of the entire system and the tube will equalize at a pressure of 22 cm of mercury.
14. Remove the tube from the vacuum line and place in the lead pig and count as described in Section V.
15. Remove the generator and replace it with a freshly charged generator. Close stopcock 1 and open stopcock 2. Place a counting tube on the right side of the manifold, open stopcock b and 4 and evacuate the manifold while counting the filled tube.
16. Wash the used generator by taking apart and flooding the bottom with water. Rinse out the spent calcium. Soak

both parts of the generator for several hours in kerosene to remove the Apiezon N grease. Wash the generators with Alxonox and water (with scrubbing). Rinse well and dry in an oven. The generators must be thoroughly dry before use to prevent reaction with the calcium metal.

III. Counting the Sample

Since satisfactory plateaus have not been obtained with the type of tube filling used in this procedure, it is necessary to count the tritium in the proportional region of the plateau curve at an exact and reproducible voltage above the starting potential. It has been found that 50 volts above the starting potential gives satisfactory and reproducible counting rates.

1. Place the GM tube (filled with gas from the sample) in the lead pig, with the anode in contact with the high-voltage lead from the sample scaler. Clip the ground lead from the sample scaler to the cathode.
2. Turn on the high voltage on the background and sample scalers.
3. Set the universal timer for 30 seconds.
4. Turn on the count switch on the control panel.
5. Turn the high-voltage adjustment up slowly on both scalers until the counter just starts to count. Note the reading on the voltage scale and check the point

several times by approaching it from both sides. Set the high-voltage adjustment at the point where the scaler just starts to count.

6. Add 50 volts to both counters with the preset addition switches on the scalers.
7. Reset the registers on both scalers to zero and reset the interpolation lights with the reset button on the control panel.
8. Set the timer for two minutes.
9. Turn on the count switch on the control panel.
10. Count the sample and the background tubes for two minutes and record each count. The count is obtained by multiplying the figure on the register by 100 and adding to this the count on the interpolation lights.
11. Count the sample until the observed single counts, obtained by subtracting the background count from the sample count and dividing this net count by the number of minutes counted, do not differ by more than one standard deviation from the average net count. (See example.)

Example: (Two-minute counts)

	<u>Sample Count</u>	<u>Background Count</u>	<u>Net Count</u>	<u>Net Count/ Minute</u>
1st Count	900	702	198	96
2nd Count	1035	815	220	110
3rd Count	950	742	208	104
Average net count per minute				103
Standard Deviation ($\pm >103$)				10

Average net count per minute $\pm$ standard deviation = 93 to 113 counts per minute. The three counts given in the example fall within the range from 93 to 113 and are acceptable counts. If in three or more counts, one is far outside the average range, as given above, it is permissible to discard that count in computing the average.

12. The results are reported in $\mu\text{c/liter}$.

$$\frac{\text{Average net sample count per minute} - \text{GM tube background}}{\text{tube standardization factor}} =$$

$\mu\text{c/liter}$ of tritium

13. When the count is completed, turn the voltage down with the high-voltage adjustment and turn the high voltage off on the sample scaler. Remove the GM tube.
14. Place the sample GM tube on the vacuum line and evacuate it. The tubes are evacuated between each filling. They should not be allowed to stand for any length of time with a filling in them.

IV. Procedure for Shutting Down the Apparatus

1. Evacuate all the GM tubes.
2. Open stopcock 2 and 4 so that the entire vacuum line is at atmospheric pressure.
3. Turn off the Cenco Hyvac pump.
4. Remove the Dewar Vessel from the first trap. Take this trap off the line. When the trap has thawed, clean and dry it.

5. Close both valves on the ethylene and argon cylinders.
6. Turn off the high voltage on both scalers. Then turn off the master switches on both scalers. Turn off the AC switch on the control panel.

V. Calibration of the Manometer

The manometer settings referred to in Section II were determined with a single gas -- usually ethylene.

1. Evacuate the right side of the manifold with the counting tube in place and open. Note the level of the mercury in the manometer when the system is evacuated.
2. With needle valve c, add ethylene until the pressure in the system is 15 cm of mercury. The pressure in the system is measured by the difference in level between the mercury in the arms of the manometer.
3. Close stopcock b.
4. Add ethylene until the pressure is approximately 19 cm of mercury. Open stopcock b to allow the pressure to equalize in the tube and the system. The pressure should now be about 17 cm of mercury.
5. Repeat steps 2, 3, and 4 until a manometer reading is obtained which allows the pressure in the tube to increase by exactly 2 cm of mercury. Note this reading.
6. Fill the system (and the tube) with ethylene until the pressure is at 17 cm of mercury. Close stopcock b.
7. Add ethylene until the pressure is approximately 27 cm

of mercury. Open stopcock b and allow the pressure in the system to equalize. The pressure should now be about 22 cm of mercury.

8. Repeat steps 6 and 7 until a manometer reading is obtained which allows the pressure in the tube to increase by exactly 5 cm of mercury. Note this reading.
9. The manometer settings thus obtained can be used until the volume of the system is changed.

VI. Counting Tubes

A. Preparation of Tubes

The counting tubes are made with a 200-ml volume, according to specifications at LASL of lime glass with a 1-mil stainless steel center wire. The center wire has a hood at each end. On one end it is fastened to a small stainless steel spring. At each end of the tube is a 20-mil platinum lead (fused with the glass) which extends at least 1 inch beyond the end of the tube and approximately 1 inch inside the tube. The inner ends of the leads are hooked. One lead is hooked to the stainless steel spring and the other to the center wire. The metal-to-metal connections are secured with a silver solder. The outside of the tube is coated with a silver mirror which serves as the cathode.

1. Wrought copper tube caps (3/8" ID) are procured from stock and a small hole drilled in the end of the cap. The cap is partially filled with Armstrong's cement and

placed over the end of the glass tube with the center wire through the hole. When the cement is thoroughly set and the cap firmly fixed on the tube, the protruding wire is clipped off and sealed to the cap with a drop of solder.

2. The tube is cleaned by rinsing with 15 ml of concentrated nitric acid. Rinse five or six times with distilled water and wash with a weak solution of Alconox. Rinse thoroughly with distilled water to remove all the detergent and then rinse twice with ethyl alcohol. Dry by placing the tube on the vacuum line and pumping for several hours. Wash and polish the outside of the tube.
3. The tube is silvered on the outside with Brashear's Silvering Solution. (Strong, John, "Procedures in Experimental Physics", pp 152-157, Prentice-Hall, New York, 1938.)

Reagents

Ammonium Hydroxide - 28%, sp gr, 0.90

Silver Nitrate Solution I - 20 g silver nitrate crystals in 300 ml distilled water.

Silver Nitrate Solution II - 60 g silver nitrate crystals in 180 ml distilled water. This quantity should be in excess of that needed for the solution.

Potassium Hydroxide Solution - 14 g potassium hydroxide in 100 ml distilled water.

Dextrose Solution - 7.8 g dextrose in 120 ml distilled water. This quantity of solution is sufficient for two tubes. The tube surface must be absolutely clean.

- a. Place silver nitrate solution I in a large beaker with a magnetic stirrer and add ammonium hydroxide solution until a dark brown precipitate of silver oxide forms and the solution begins to clear.
- b. Continue adding ammonium hydroxide dropwise until the solution just clears.
- c. Add silver nitrate solution II dropwise until the solution is a distinct straw color.

DANGER -- USE GOGGLES

- d. Add slowly with constant stirring the potassium hydroxide solution.
- e. Add ammonium hydroxide dropwise until the solution just clears.
- f. Add silver nitrate solution II until there is a thin straw or brown precipitate. Disregard small flecks.
- g. Filter the solution through glass wool.
- h. Place the tube to be silvered in a glass cylinder long enough so that the tube will be immersed to the shoulder. The tube should be supported. The ends of the tube are covered with masking tape and then coated with paraffin (by dipping in melted paraffin)

to keep them from being silvered.

- i. Mix one-half the dextrose solution with one-half the filtered solution and immediately pour over the counting tube. Let stand until the mirror forms. (1-2 minutes.)
 - j. Remove the tube, rinse thoroughly with distilled water and let dry overnight.
 - k. With the other halves of the two solutions, immediately plate a second tube.
 - l. When the tube is dry, plate again with silver solution as given above. Each tube should have two coats of silver.
 - m. Discard all silvering solutions immediately by pouring down the sink and flooding with water. These solutions are extremely hazardous and under no circumstances should they be stored.
4. After the tubes have been plated and the paraffin cleaned off, place a strip of copper foil (20 mil, 3/8" x 3-1/2) in contact with the silver mirror. 2-1/2" of the strip should be in contact with the mirror. Fasten the strip in place with scotch electrical tape. Wrap the entire mirror, tightly, with scotch electrical tape to protect the plate. 1" of the copper strip extends beyond the wrapping and serves as a lead to which the ground lead from the scaler is clipped.

5. Number each tube with a distinctive number.

B. Counting Tube Backgrounds

1. Fill each tube with inert hydrogen generated from distilled water, using the procedure given in Section II.
2. Count as given in Section III. Obtain a sufficient number of counting rates so that the tube backgrounds do not differ by more than the standard deviation. (Section III)
3. The difference between the counts per minute of the background tube and the counts per minute of the new tube is known as the tube background. (Expressed in counts per minute.)

New sample tube	360 c/m
Background tube	<u>345</u>
Tube background	15 c/m

4. The background tube should be chosen so that its counting rate is lower than that of the sample tubes.
5. The tube background changes with use. It should be rechecked every week or two or after being filled with samples with extremely high tritium concentrations. If the tube background is more than 30 c/m the tube should be recleaned until the background drops to 30 c/m or less.

C. Tube Standardization Factor

The tube standardization factor gives the number of counts per minute for each microcurie of tritium in a

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liter of tritium standard. The factor is expressed in terms of counts per minute per microcurie per liter of tritium.

1. Fill each tube with tritium generated from the working tritium standard (tritium = 20 $\mu\text{c/liter}$) using the procedure given in Section II.
2. Count as given in Section III.
3. Calculate the tube standardization factor.

$$\frac{\text{Average net count per minute} - \text{tube background}}{20 \mu\text{c/liter}} =$$

tube standardization factor $\text{c/m}/\mu\text{c/liter}$

Example:

$$\text{Average net c/m } 700 \text{ c/m } \frac{700 \text{ c/m} - 20 \text{ c/m}}{20 \mu\text{c/liter}} = 34 \text{ c/m}/\mu\text{c/liter}$$

Tube background 20 c/m

□ tube standardization factor

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DETERMINATION OF MERCURY IN URINE AND AIR

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It is almost inconceivable that an element known for centuries should appear on the same program with such notables as tritium, plutonium, polonium, and uranium. The title hygrargyrum would at least place the element in a much closer companionship to these more "excited" elements.

The determination of mercury in urine is still a problem. We have not fully answered the questions of digestion of organic matter, absolute identification in microgram quantities or a practical method of determining these quantities. Since the turn of the century, some 200 methods for the determination of mercury in biological fluids have appeared in the literature. In contrast to these early methods, we have answered these questions within the limits of our knowledge.

The normal excretion of mercury in urine varies from 0.005 to 0.050 mg of mercury per liter. This wide range is misleading but is becoming more narrow as the use of mercury compounds in our daily life becomes smaller. The normal usually considered is 0.010 mg of mercury per liter of urine. The isolation of mercury from urine has been accomplished by many techniques. Table I illustrates those precipitation techniques which have been employed for the direct isolation of mercury from urine.

TABLE I

DIRECT ISOLATION OF MERCURY FROM URINE BY PRECIPITATION

Direct precipitation as the sulfide	
	oxide
	complex iodide
Coprecipitation	as the oxide with calcium phosphate
	calcium carbonate
	barium sulfate
	albumin
	as the sulfide with copper
	cadmium

None of these methods are practical or quantitative.

Table II illustrates those miscellaneous methods of direct isolation of mercury from urine which are probably the least desirable.

TABLE II

DIRECT ISOLATION OF MERCURY FROM URINE BY MISCELLANEOUS METHODS

Extraction with ethyl acetate after converting mercury to mercuric iodide.

Distillation of mercury from an acid solution with chlorine gas

from potassium chlorate and hydrochloric acid

from sulfuric acid

Special method spectrographic examination of urine by spray techniques

The third method has proven satisfactory for those workers who consistently excrete over 0.05 mg Hg/liter.

Table III shows those methods of isolating mercury direct from urine by electrodeposition.

TABLE III

DIRECT ISOLATION OF MERCURY FROM URINE BY ELECTRODEPOSITION

	<u>Electrodes</u>	<u>Form</u>
With our applied current	copper aluminum	wire, foil, etc. foil
With applied current	gold zinc aluminum platinum carbon copper copper	wire, foil rod foil foil rod wire, foil (Nascent Cu from a CuSO ₄ Solution)

Most of these approach complete recovery of the mercury but are time-consuming and usually increase the contamination problem for the more delicate determinations. Most of the isolation techniques illustrated are at best semi-quantitative. Several of the techniques are applicable to oxidized urine.

The removal of organic matter has been a point of discussion for some time due to the volatility of mercury and its compounds. The use of open vessel techniques is obviously impractical as well as those distillation methods previously mentioned.

Table IV illustrates those methods which are being employed to digest or oxidize the organic matter of urine prior to isolation and analysis. All of these are carried out under a water reflux condenser.

TABLE IV

OXIDATION OF URINE FOR MERCURY ANALYSIS
(Refluxing Techniques)

Agents

HNO₃ followed by H₂SO₄ and KMnO₄

KClO₃ and HCl

HNO₃ and KMnO₄ (10 ml:7 gm)/100 ml urine (ACGIH)

H₂SO₄ and K₂S₂O₈

H₂SO₄ and H₂O₂

H₂SO₄ and HNO₃ (1:1) 30 ml/100 ml urine (AOAC)

H₂SO₄ and KMnO₄ (10 ml:4 gm)/100 ml urine (LASL)

Hubbard reports that no loss in mercury is observed when an air condenser is used. The AOAC method is very cumbersome for routine use and losses are observed due to incomplete washing of the apparatus. Figure 1 (Note 1) shows the Soxhlet reflux assembly.

As the urine boils, the water is distilled to the 85-ml Soxhlet extraction chamber, at which time the concentrated acids act on the nonvolatile organic material. Figure 2 illustrates the type of assembly being employed at Los Alamos, which is similar to that recommended by the ACGIH.

We use sulfuric acid and potassium permanganate in this assembly and have found it to be superior to any of the methods published.

This procedure is as follows:

Note 1: The figures for this section of the report are not available.

Add 4 g of KMnO_4 to 100 ml of urine and allow the solution to stand under the reflux system for at least 15 minutes. This preliminary oxidation prevents frothing at later stages. Ten milliliters of sulfuric acid is added over a 3-5 minute period and then the urine is refluxed for 30 minutes to one hour at a vigorous boil. The heater is removed and hydroxylamine sulfate is added until all the manganese dioxide has been reduced. The flask is allowed to cool in the reflux assembly until it is at room temperature. The contents are partially neutralized to a pH of 2 by a predetermined amount of NH_4OH . The flask should remain connected to the condenser until the analysis is to be continued.

In addition to those isolation techniques previously mentioned, some form of extraction procedure is being used by most laboratories. However, several laboratories are using a modification of Stock's Method, which is the distillation of mercury from copper and measuring the mercury globule or column in a capillary tube. The AOAC and ACGIH methods are both modifications of previously published dithizone procedures. The titrametric method still appears in the literature but lacks the sensitivity necessary for urine analysis. Di-~~B~~-naphthylthiocarbazone has several advantages over dithizone but is more sensitive to interferences.

I would like to limit the remainder of this discussion to the dithizone methods.⁽¹⁾ The primary criteria for extracting with dithizone is that mercury must be extracted in an acid solution for better specificity. To further remove interfering elements, the

thiocyanate ion is added. Re-extraction of the organic phase with an excess bromide is the main step in the AOAC and ACGIH methods. Recently, the use of versenes and, in particular, sodium versenate are combined with the acid pH and thiocyanate to make the methods specific.

In our Laboratory, the oxidized urine is quantitatively transferred to a beaker after it has reached room temperature. The solution is then made more alkaline by adding ammonium hydroxide until the pH meter reads between 5.5 and 6. Five milliliters of 5 per cent sodium versenate and 5 ml of 5 per cent potassium thiocyanate are added. The solution is then titrated with a citrate-phosphate buffer to a pH of 4. This is then transferred to a separatory funnel. Ten milliliters of a 4 mg dithizone solution of CCl_4 is added and shaken for one minute. The carbon tetrachloride phase is then drained into a Coleman cuvette and the per cent transmission determined at 490 mp. The quantity of mercury present is then determined by referring to a similarly prepared standard curve.

The various methods for measuring the concentration of the mercury dithizonate in a dithizone extract are shown in Table V.

TABLE V

COLORIMETRIC MEASUREMENT OF MERCURY IN A DITHIZONE SOLUTION

Mixed color method	single reading	Hg D _{zn} 490 mμ.
Single color method	single reading	Removal of excess DZN by ammonium hydroxide. Hg D _{zn} 490 mμ.
Mixed color method	double reading	Hg D _{zn} 485 mμ. D _{zn} 620 mμ. Differences plotted vs. concentration.
Reversion method	double reading	Single color method or mixed color method followed by reversion of the metal dithizonate. Differences plotted vs. concentration.

The first method is certainly the simplest, but has the possibility of errors due to the volatility of the solvent and changes in the dithizone concentration due to light and oxidation. Therefore, even a standard analyzed at the same time as the unknown sample may vary from an earlier prepared curve. This error lies between 95-100 per cent of the previously analyzed standard. If good laboratory techniques are employed, the upper value is constant. Besides these errors, the second method shows a loss of mercury due to the additional extraction which may cause a considerable loss of mercury. Agents such as iodine in potassium acid phthalate are used. The third method virtually eliminates the errors previously mentioned. However, the ratio of dithizone to mercury dithizonate is critical and must be prepared with caution. The fourth method is perhaps the greatest advance in colorimetric

analysis, particularly with dithizone. The precision of any method would be improved but the accuracy would remain approximately the same. We found no great advantage in employing this method of analysis to the simple method previously discussed.

I believe it is a well-established fact that the concentration of mercury in the urine is not a basis for predicting the worker's exposure to mercury vapor. Cases are reported where the urinary level is only slightly raised and a serious mercury poisoning exists. The psychological barrier of blood specimens prevents us from routinely using this fluid in our industries. Chemical changes in the urine as a criterion for mercury vapor exposure are vague and, for the most part, are only significant after gross damage has occurred. The albumin determination has gained favor but is only of value because of the damage to the kidneys. So far, no laboratory procedure has been developed which indicates either the degree of mercury exposure or the total mercury intake. The question of "why determine urinary mercury?" will arise so the need of any discussion is unnecessary.

The determination of mercury in air has had less attention in the last few years. The search for more precise methods has been de-emphasized since several commercial instruments are available. However, several laboratories still revert to sampling of the air with bubblers or impingers. Some of the absorption solutions are shown in Table VI.

TABLE VI

ABSORPTION AGENTS FOR MERCURY VAPOR

<u>Common Solutions</u>	<u>Less Common Solutions</u>	<u>Other Methods</u>
0.1N H_2SO_4 and KMnO_4	Boiling HNO_3	Liquid N_2 or air trap
Dil. HNO_3 and KMnO_4	Aqua Regia	CO_2 in ether trap
<u>0.25% I_2 in 3% KI</u>	10% SnCl_2 in 5% HCl	Glass spiral coated with I_2

The solution underlined is perhaps the most common and is still being used for calibration analysis in most laboratories. This solution of the mercury may be followed by any method for determining the mercury content.

A number of devices have been employed for the detection of mercury vapor. Some of these agents are commercially available but for the most part are made in the laboratory. Table VII shows some of the more sensitive agents which are in use.

TABLE VII

CHEMICAL DETECTORS FOR MERCURY IN AIR

Selenium sulfide on paper

Selenium sulfide activated by precipitation from AlCl_3

Potassium selenocyanide on paper after exposure to HCl

Potassium selenocyanate on paper after exposure to HCl

Cuprous iodide on silica gel

Aluminum chloride on silica gel

Physical methods of demonstrating mercury vapor are currently being used. Doctor Charles R. Williams of the Liberty Mutual Insurance Company in Boston recommends the use of Sylvania phosphor screens and a portable mineral light to educate the chemist and physicist that mercury vapor is present. These shadows vividly demonstrate the volatility of mercury from remote places. These screens can be prepared by using anthracene.

Various semiquantitative methods can be found. The older methods, such as those originally designed by General Electric, used either the visual comparison of a selenium sulfide paper or, later, the photoelectric estimation using the same agent. Some laboratories have made their own ultraviolet absorption instruments, employing a 4-watt germicidal lamp and various types of photocell circuits. The portable commercial instruments available operate on the principle that mercury vapor absorbs the $2536\text{\AA}$ resonance line from a mercury vapor lamp. Table VIII shows the order of usage of these instruments by the industrial hygienist. The last two instruments operate on a much more complicated circuit. All the instruments are affected by ozone, dust, smoke, and to some extent, various organic vapors.

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TABLE VIII

PORTABLE PHOTOELECTRIC MERCURY VAPOR DETECTORS
(in order of usage by the industrial hygienist)

<u>Manufacturer</u>	<u>Sensitivity mg/M³</u>	<u>% of Scale for M.A.C.</u>	<u>Alarm System</u>	<u>Weight (lb)</u>
General Electric (A)	0.05	10	No	25
Harold Kruger (1)	0.03	5	No	5
(2)	0.005	100		
	0.03	5	No	7
(3)	0.03	5	Yes	8
Lermac, Inc.	0.01	10	Yes	28
U.C. Radiation Lab.	0.001	100	Yes over	30

Note: Interference from ozone, dust, smoke, etc., increases as the instrument is made more sensitive.

Los Alamos employs the General Electric mercury vapor detector. A preliminary check in the laboratory prior to field use is important. An MSA Mersorb cartridge is used as a zero in contaminated atmospheres. If the sampling tube becomes contaminated, a zero check under operating conditions will cause a definite deflection of the meter.

SUMMARY

A method was reviewed for determining mercury in urine. The method is simple and well within the wide range of mercury excretion levels from the normal to the abnormal. The need for a better method of determining the worker's exposure to mercury has been pointed out. The analysis of the workroom air has been simplified by photoelectric mercury vapor detector devices.

REFERENCE

Campbell, E. E. and Head, B. M., The Determination of Mercury by Single Extraction, LA-1886, March, 1955.

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THE NATURAL RADIOACTIVITY OF MAN

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During the last five years, new information has become available on the radioactive content of man living in the average environment. This knowledge is of concern to two professional groups working in the field of applied atomic energy. It is of concern to the health physicist, since it forms the baseline for his maximum permissible level estimates. It is of concern to the bio-assayist, since it determines the blank or background for his radiochemical or physical measurements. In deference to the interests of the group assembled here, my presentation of the subject shall seek to stress implications for bio-assay work. Therefore, what I have to say is organized under two general headings. First, we shall endow the standard man with what we believe to be his proper radioactive attributes and then, we shall inquire as to how these radioactive qualities influence the measurements of interest to the bio-assayist.

As you know, our natural radioactive environment includes the three radioactive series, headed by uranium, actinium, and thorium. Of the single naturally radioactive isotopes spotted throughout the list of elements we shall need to consider only C^{14} and K^{40} . It is generally recognized that if we go out in the fields and grab up a handful of soil, that handful contains all these radioactive materials. It is perhaps less commonly appreciated that the books we read, the

chairs we sit in, the house we live in, the food and water that we drink, all contain these naturally occurring materials. Since man is a dynamic organism, he is constantly incorporating part of this environment into his muscle, bone and other body organs. Since he and other living animals and plants are somewhat discriminating in the elements they pick up, man's radioactive content is not identical with that of the handful of dirt. At this point, I would like to point out a difference in the behavior of C^{14} and K^{40} as contrasted with Ra^{226} . These three isotopes comprise the principal subjects of the discussion to follow. As you know, both carbon and potassium are major body constituents, the radioactive C^{14} comprising about 1 in 10^{12} atoms of carbon and K^{40} comprising about 1 in 10^4 atoms of potassium. Since the discrimination of the human organism is based on chemical processes, it is to be expected that the ratio of C^{14}/C^{12} and of $\frac{K^{40}}{K^{39}+K^{41}}$ will be the same inside the body as in nature. The problem of calculating the body radioactive content of these isotopes depends simply on the total carbon and potassium body content.

The situation is different for radium²²⁶. Although not an essential body constituent, it is chemically sufficiently like Ca so that it is built into the bone mineral as a calcium substitute. Because the "wisdom of the body" sees only with a chemist's eyes and lacks the vision of a physicist, radium is actually hoarded in the bones in a concentration exceeding that of the natural food environment. To support the statement that the body hoards radium, let us look at the action in the kidney. Putnam working on dogs in my laboratory concluded that approximately 80 per cent of the circulating radium was filterable by

the kidney glomerulus, but that 90 per cent or more is resorbed in the tubules. It is because of this selection of Ra by the body that it is necessary to consider that element in discussions such as this. This concludes my general remarks. Let us proceed to a consideration of the data on body radioactivity.

I shall discuss in detail C^{14} , K^{41} , Ra^{226} , Rn, and Bi^{214} (RaC). Other radioactive elements (either because of short half-life, negligible absorption in the body, low solubility, or a combination of these factors) do not make important contributions to the total body radioactivity.

Table I presents a calculation of the C^{14} body content. The standard man is designated as having a total carbon content of 18 per cent of 12,600 grams. Libby states that there are 15 d/m/gram C due to the decay of C^{14} . The average body content may then be simply calculated as 8.5×10^{-8} curies.

TABLE I

C^{14} BODY CONTENT

1. "Standard Man" contains 12,600 G. carbon
2. 15 d/m/g. C (W.F. Libby "Radiocarbon Dating"
University of Chicago Press)
3. Body content = $\frac{15 \times 12,600}{2.22 \times 10^{12}} = 8.5 \times 10^{-8}$ curies

The decay equation is:

The emitted beta particle has an energy of 0.156 Mev and the half-life is approximately 5700 years. Since carbon is more or less uniformly distributed throughout the body, the radiation is general. The absence of a gamma ray and the softness of the beta particle cause the range of action of a single event to be within 0.1 mm or so from the origin of the beta particles.

A similar calculation may be made for K^{40} and appears in Table II. The lesser amount of potassium in the body, i.e., 245 g in the standard man, is compensated for by the greater specific activity of K^{40} as compared with C^{14} . Sawyer and Wiedenbeck find that naturally occurring potassium has 1698 disintegrations per minute per gram potassium from the beta decay of K^{40} . The calculation estimates 1.9×10^{-7} curies as the body content of K^{41} .

TABLE II
 K^{40} BODY CONTENT

1. "Standard Man" contains 245 g potassium
2. 1698 d/m/g K (Sawyer and Wiedenbeck, Phys. Rev. 79, 490) is taken as specific activity.
3. $\frac{1698 \times 245}{2.22 \times 10^{12}} = 1.9 \times 10^{-7}$ C/whole body

The decay equation of K^{40} is not verified in detail. The one presented below is that proposed by Sawyer and Wiedenbeck:

Although in a cellular sense K is distributed heterogeneously, i.e. it is approximately 30 x more concentrated inside the cells than in the extracellular fluid, in a more macroscopic sense it is distributed uniformly throughout the body. The beta particle emitted by K^{40} is an energetic 1.35 Mev and has an average range in tissue of approximately three mm. For about every 10 beta particles, there is one gamma ray. Thus, dosimetrically, potassium may be regarded as uniformly distributed throughout the body.

This brings us to the consideration of Ra^{226} , the data for which appears in Table III. The first experimental data on this subject was presented by Adolf Krebs, who obtained the ashes from 18 deceased individuals who were not exposed to radium by occupational pursuits during life. As shown in the slide Krebs used two methods of analysis. Counting the unprocessed ash with a point counter would of course include in the measurement all alpha emitters, whereas the solution of the ash and measurement of the radon evolved measures only radium-226. Krebs does not designate which method was used to obtain which result. He reports whole body radium contents of from less than 1×10^{-9} (3 cases) to 4.0×10^{-8} with an average value of 1.4×10^{-8} .

TABLE III
EXPERIMENTAL DETERMINATION OF Ra²²⁶ BODY CONTENT

SOURCE REFERENCE	BODY CONTENT IN GRAMS	SUBJECTS	METHOD
A. Krebs Strahlentherapie, <u>72</u> , 164, (1942).	1.4×10^{-8}	18 (Deceased)	Either 1) Unpro- cessed ash in a point counter. Or Radon emana- tion from solu- tion of dis- solved ash.
Hursh and Gates, Nucleon. <u>7</u> , 46, (1950).	1.2×10^{-10}	25 (Deceased in Rochester, N.Y.)	Radon emanation from solution of dissolved ash.
Palmer, Kornberg, and Queen; Personal Comm., 1954	0.47×10^{-10}	50 (Deceased in Portland, Ore.)	Radon emanation from solution of dissolved ash.
Stehny and Lucas Radiation Research Society, May, 1955.	4×10^{-10}	(16-18 yr. old boys, Lockport, Ill.)	Breath radon measurements on living subjects.
	2×10^{-10}	Prisoners, Statesville, Ill.	

We became interested in this question at the University of Rochester and obtained the ashes of 25 cadavers. They were analyzed by dissolving a 20-g aliquot, allowing the sealed solution to build up radon, which was boiled off and counted. Our results gave radium body contents which varied from 0.4×10^{-10} to 4.0×10^{-10} grams Ra²²⁶, with an average value of 1.2×10^{-10} grams. Later on, we reexamined some of these samples, separating the radium by the method of Ames, Sedlet, Anderson, and Kohman and counting the radium-barium sulphate precipitate.

in a 2 π low-background alpha counter. These results are presented in Table IV and show that the total radium content including all radium isotopes is not significantly different from the body content of Ra²²⁶ as measured by radon methods. From these findings, we conclude that the body does not contain significant amounts of the long-lived members of the thorium chain, justifying our position that it is sufficient to measure Ra²²⁶ alone.

TABLE IV

<u>SAMPLE NO.</u>	<u>RA ELEMENT (10-13 g/g ash)</u>	<u>RA²²⁶ (10-13g/g ash)</u>
8	0.52	0.40
9	0.62	0.69
10	0.36	0.33
11	0.36	0.32
12	0.28	0.30
13	0.68	0.53
14	0.38	0.39
15	0.52	0.45
16	0.66	0.64
17	0.38	0.38
18	0.31	0.25
19	0.43	0.19
20	0.26	0.26
24	0.54	0.58

Table III gives results obtained by Palmer, Kornberg, and Queen using the same method as Hursh and Gates. Their analysis of 50 cadavers shows values of radium-226 body content from 0.3 to 1.39×10^{-10} grams with an average of 0.47×10^{-10} grams.

Stehny and Lucas of Argonne laboratory have measured radon in the expired air of occupationally unexposed living subjects (Table III). Results are quoted in the table for two age groups, 16-18 year old boys from Lockport, Ill. and a group of prisoners at Statesville, Ill. These two communities are both served with drinking water in which the natural Ra^{226} content is considerably higher (by a factor of about two orders of magnitude) than the average value for large cities in the United States. The boys drink water containing 8×10^{-12} g Ra^{226} per liter and have an average body content of 4×10^{-10} g Ra^{226} , whereas the prisoner group drinks water containing 3.4×10^{-12} g per liter and have an average body content of 2×10^{-10} g Ra^{226} . The simple statement that these measurements were made is incomplete without a passing tribute to the meticulous technique necessary to measure radon concentrations in the expired air which are approximately 1/100th of the natural radon concentration in the surrounding air.

Without further discussion at this time, I should like to sum up by stating a personal opinion that the average radium body content of man is of the order of 10^{-10} gram and is probably between 1×10^{-10} and 2×10^{-10} gram. I doubt if there are an appreciable number of individuals (unexposed to radium occupationally) who have radium body contents in excess of 6×10^{-10} g am. This radium body load is concen-

trated in the skeleton. It has been shown to be unevenly distributed in the microscopic sense so that "hot spots" exist with a concentration of 10 times the average radium concentration.

Table V presents some calculations on the radon body content of man. I should perhaps be careful to state that the radon we are talking about at this point is the naturally occurring radon in the environmental air and we shall in this calculation not concern ourselves with the radon evolved from radium deposits in the body. For the purposes of the calculation, the radon concentration in the air is assumed to be 0.2×10^{-12} curies radon per liter. The partition coefficient (α) is defined as the ratio of the concentration per unit volume in the material in question to the concentration in the air with which it is in equilibrium. The coefficient for body tissues in general is taken as 0.2, for body fat as 5.0. The standard man is estimated at a volume of 70 liters, his fat at a volume of 6 liters. The calculation then assigns a total radon content of 8.6×10^{-12} curies to the average man. This is small in comparison with the other previously outlined sources of natural radioactivity in man. I have considered it here for two reasons. The first is that the natural level of radon may be quite variable. There are communities in the Colorado Plateau region where the radon level in the air may be two or three orders of magnitude higher than that assumed for the calculation. The second reason is that in human bio-assay, the radon level of the air must be taken into consideration, as will be revealed later in the discussion.

TABLE V

RADON BODY CONTENT

1. Assume 0.2×10^{-12} curies Rn per liter in air.
2. Assume average partition coefficient, α , for body tissues (except fat) as equal to 0.2;
 α for fat = 5.0
3. Volume standard man = Ca. 70 liters
Volume Fat = Ca. 6 liters
4. $0.2 \times 10^{-12} \times 0.2 \times 64 = 2.56 \times 10^{-12}$ curies
 $0.2 \times 10^{-12} \times 5 \times 6 = 6 \times 10^{-12}$ curies
Total radon content = 8.6×10^{-12} curies

The fifth and last source of body radioactivity that I will discuss is RaC. As an introduction to this discussion, we shall refer to the decay chart of the uranium series as shown in Figure 1. It will be noted that radon decays into a series of shortlived daughters. In the atmosphere, these daughters deposit on small particles in the air. When inhaled into the lung, these daughter-bearing aerosols deposit on the moist surfaces of the air passageways and the alveoli. The lung therefore acts somewhat like a scrubbing tower and serves to clean the air of daughters. As a consequence, the concentration of daughters in the lung increases until the rate of daughter decay (by particle emission) is just equal to the rate at which new daughters are added by the breathing process. As may be seen from the chart RaC (Bi^{210}) has a very short half-life alpha-emitting daughter, which in turn decays to the 22-year half-life Pb^{210} .

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FIGURE 1 DECAY CHART OF THE URANIUM SERIES

Although we shall calculate the lung content of RaC, a beta-emitter, it is the short half-life daughter, Po^{214} , that is of greater significance dosimetrically speaking, since it emits an energetic alpha particle. However, because of its short half-life, its rate of disintegration is the same as that of RaC and stipulating the activity concentration of the latter identifies Po^{214} content as well.

Table VI presents this calculation. Assuming that 1) the air concentration of radon is 0.2×10^{-12} curies per liter with the daughters in equilibrium, 2) that 25 per cent of the daughters are retained in the lung, 3) that the breathing rate is 20 liters per minute, we estimate the lung RaC content as 6.7×10^{-11} curies. For the present, it may be noted that although the RaC content in curies is considerably less than that of K^{40} or Cl^{14} , when the level is multiplied by 20 (for R.B.E. of alpha) by 7 (K^{40}) or 60 (Cl^{14}) (to allow for particle energy differences), when modified by consideration of the fact that the radiation from RaC is confined for the most part to the lung, (about 1/70th of the total body weight) and taking due account of possible higher natural atmospheric levels of radon, the lower value for RaC becomes of dosimetric interest.

Table VII summarizes the radioactivity of human subjects. It is seen that in total number of disintegrations per minute, K^{40} and Cl^{14} are considerably higher than the other sources. In terms of biological effectiveness, the heterogeneously distributed, alpha emitting Ra^{226} and RaC (+ Po^{214}) assume a more important position. Since we are not primarily concerned here with dosimetric considerations, let

us leave it at that and proceed to a consideration of how the presence of these radioactive sources in man affect bio-assay measurements.

TABLE VI

RADIUM C BODY CONTENT

1. Assume 0.2×10^{-12} curies Rn per liter average air, daughters in equilibrium.
2. Assume 25 per cent of inhaled daughters are retained.
3. Breathing rate = 20 liters per min (standard man)
4. RaC (in lung) formed from deposited RaB

$$= \frac{0.2 \times 10^{-12} \times 0.25 \times 20 \times 26.8}{0.693} = 38.6 \times 10^{-12} \text{ curies.}$$

RaC (in lung) deposited from air respired

$$= \frac{0.2 \times 10^{-12} \times 0.25 \times 20 \times 19.7}{0.693} = 28 \times 10^{-12} \text{ curies}$$

= Total body content = 6.7×10^{-11} curies.
 (Concentrated principally in lung.)

TABLE VII

SUMMARY OF NATURAL BODY RADIOACTIVITY

MATERIAL	AVG BODY CONTENT IN CURIES	DISTRIBUTION
K ⁴⁰	1.9×10^{-7}	Uniform
C ¹⁴	8.5×10^{-8}	Uniform
Ra ²²⁶	1.5×10^{-10}	Bone
Radon	8.6×10^{-12}	2/3 in body fat
RaC	6×10^{-11}	Lung

The bio-assayist looking for radioactivity in a human subject may use one or all of five approaches. He may obtain biopsy samples, he may collect and measure expired air, or urine or feces. If he has available suitable equipment, he may make whole-body gamma ray surveys. Let us attempt to predict what the results would be were he to apply the above methods to the standard man equipped with the standard radioactive accessories as outlined in the previous section.

The situation with biopsy samples is readily estimated on the basis of the data of the last slide. The beta activity will be approximately $\frac{2.74 \times 10^{-7} \times 2.22 \times 10^{12}}{7 \times 10^4} = 8.7$ d/m/gram wet weight. If the sample is bone, one might expect an alpha activity of $\frac{1.5 \times 10^{-10}}{7000} \times 2.22 \times 10^{12} = 0.048$ d/m/gram from Ra²²⁶. Depending on whether radon is retained in the counting preparation, the above count may be augmented as much as four times. The other body sources in most cases would make negligible contributions to the biopsy tissue count.

The analysis of the expired breath is a useful monitoring procedure for body radium or thorium loads. The arrangement for counting the radon gas necessarily must be beta and gamma insensitive, since a low background is required to measure the low level alpha activity. For this reason, the presence of C¹⁴O₂ in the expired air of the standard man (0.3 d/m/liter) will create no measurement difficulties. The presence of radon in the air in amounts equivalent to 10 per cent or more of the net radon expired per liter by a subject bearing maximum permissible level of radium-226 (= 0.1 µg) is the principle source of

difficulty in this measurement. The standard man will give off radon from his radium load in amounts of 0.0015 d/m/liter. It is readily seen that the atmospheric radon (equivalent to 0.45 d/m/l for 0.2 μpc /liter) with which the subject has come into equilibrium is a much more important source of background error. The way in which this error is circumvented is to require the subject to breath radon-free air from a tank for a sufficiently long period so as to blow off all of the body-stored radon.

The measurement of thoron in the respired air depends on measurement of the aerosol-borne daughters and likewise would at low levels be interfered with by naturally occurring atmospheric daughters.

The measurement of urine is one of the most convenient and commonly used methods of bio-assay. The major radioactive beta-emitting constituents in the urine of the standard man will be K^{40} , contributing 3400 d/m/24-hr sample, and C^{14} , contributing 123 d/m/24-hr sample. The alpha particle background will come from the fraction of ingested Ra^{226} which is not fixed in bone, for the most part, and may be calculated to be approximately 0.2 d/m/24-hr sample. In the measurement of urine for monitoring purposes, it is perhaps usual to separate out the element to be measured. Experiments on normal subjects separating out Po^{210} from the urine gave results which were in all cases less than 0.1 d/m/24-hr sample.

The use of fecal analysis presents sufficient inconvenience in collection and suitable aliquoting as to make it an infrequently used bio-assay method. It is simple enough to do on paper and it is in that way that we shall treat the feces of the standard man. Since the

potassium daily excretion is about 0.2 gram, the beta particle activity from this source will be 320 d/m. The carbon in the feces amounts to approximately 13 g/per day and therefore contributes 190 d/m to the 24-hour fecal sample. The alpha particle content derives from Ra^{226} and altogether is estimated at approximately 2 d/m per 24-hour sample.

Only a small fraction of this excreted radium is derived from radium fixed in the body. The remainder is either unabsorbed or rapidly excreted radium and is calculated by approximating the daily intake of radium in food and water and assuming that the amount excreted is roughly equal to the amount ingested. It is further assumed that 90 per cent or more of the radium is excreted via the feces. In regions of high natural radium content of the drinking water, these figures for α particle content need to be revised upwards.

The last method of bio-assay to be considered is that of whole body gamma survey. I have had no personal experience with this method and shall for that reason make my remarks brief despite the increasing use of this method of analysis. At least three laboratories have developed equipment which include enclosures sufficiently large to accommodate a human subject. Sievert, working in Stockholm, Sweden, published a preliminary account of results with a pressure ion chamber. In results with his chamber, there is a rough equivalence between gamma radiation from 10^{-8} gram of radium and the gamma radiation from the normal incidence of K^{40} in the body. The presence of K^{40} in our standard man, therefore, would contribute more than 98 per cent of the total gamma activity measurement. I should remark parenthetically that

Sievert interprets his measurements as indicating an average radium content of a 50-year old resident of Stockholm (?) as 8×10^{-9} g radium. I do not agree with this interpretation for reasons too involved to go into in this brief presentation.

The second α measuring equipment which we may mention is that built by Burch and Spiers working at the University of Leeds. They also used the high-pressure ionization chamber technique. If they assume that all the gamma radiation comes from K^{40} , they find that the mean potassium content of their subjects calculated from their measurements agrees satisfactorily with body potassium determination by chemical methods.

The third equipment to be described is that built at the Los Alamos laboratory by Reines and collaborators. They employed a tank surrounded by a liquid scintillator and a photo-multiplier tube array. The "clean" subjects that they tested gave gamma counting rates which could adequately be accounted for by the subjects' K^{40} content.

I have summarized the estimates of expected bio-assay measurements in Table VIII.

TABLE VIII

ESTIMATES OF BIO ASSAY RESULTS ON THE STANDARD MAN

	Biopsy d/m/g Wet	Breath d/m/l	Urine d/m/24 hr.	Feces d/m/24 hr	Survey
K^{40} (Beta & Gamma)	6	none	3400	320	98% total activity
C^{14} (Beta)	2.7	0.3	123	190	
Ra^{226} (Alpha & Gamma)	0.05	0.0015 (body radium) 0.45 (atmos. radon)	0.2	2	Not measur- able by existing equipment.

In closing it should be remarked that we have perforce neglected contamination by chemical reagents, storage vessels, etc. These may be real hazards in carrying out low-level analyses and deserve the attention of the analyst. If we have arrived at any conclusion, it perhaps might be stated as follows: Natural radioactivity is usually several orders of magnitude below the levels measured in bio-assay work. There are special circumstances in which a recognition that man has a natural radioactive content is important in carrying out and interpreting low-level analyses.

DETERMINATION OF MICROMICROGRAM QUANTITIES OF RADIUM

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Methods for the determination of micromicrogram amounts of radium of mass number 226 may be divided into two general categories, based on whether the radium itself is separated and counted together with its daughter nuclides, or whether the first descendent of radium, the rare gas radon, is separated and counted together with its daughters. Using either general method, it is necessary to consider the growth and decay of radium daughters in order to calculate a result. The radium disintegration chain is shown in Table I. Radium decays by alpha particle emission to a rare gas, radon, which in turn goes through the series of successive transformations shown until the stable nuclide, Pb^{206} , is produced. For analytical purposes, it is necessary to consider only that portion of the chain through RaC' , since the activity due to $22y\ RaD$ (and therefore RaE and RaF) produced during the time required for a radium analysis is negligible. The activity due to the $RaDEF$ series must be considered only when counting aged radium samples without preliminary separations.

TABLE I
Radium Decay Series

<u>Name</u>	<u>Nuclide</u>	<u>Half Life</u>	<u>Particle</u>
Radium	$^{88}_{\text{Ra}}226$	1600 y	alpha
Radon	$^{86}_{\text{Rn}}222$	3.825 d	alpha
Radium A	$^{84}_{\text{Po}}218$	3.05 m	alpha
Radium B	$^{82}_{\text{Pb}}214$	26.8 m	beta
Radium C	$^{83}_{\text{Bi}}214$	19.7 m	beta
Radium C'	$^{84}_{\text{Po}}214$	1.6×10^{-4} s	alpha
Radium D	$^{82}_{\text{Pb}}210$	22 y	beta
Radium E	$^{83}_{\text{Bi}}210$	5.02 d	beta
Radium F	$^{84}_{\text{Po}}210$	138 d	alpha
Radium G	$^{82}_{\text{Pb}}206$	stable	

One of the earliest, and still most widely used of the methods for the determination of radium consists of separating the radon produced by the unknown amount of radium and measuring the radioactivity of the radon and its alpha-emitting daughters. Since the rate of production of radon from radium is accurately known, the amount of radium can readily be obtained from the daughter activities. The rare gas properties of radon make it easily separable from both inactive solids and radioactive nuclides, and since all other emanations are short-lived, the separation and measurement of radon provides an excellent method for the determination of Ra^{226} . Many systems have been described for the determination of radium by this emanation method. ⁽¹⁾ The references are by no means complete, but are representative of the systems used. It is convenient to divide discussion of the procedure into three steps: (1) preparation of the sample, (2) separation of radon, and (3) measurement of the radon and daughter activities.

The radium-containing sample, if not in solution, is usually dissolved prior to the generation and transfer of radon to the counting chamber. The sample should be completely dissolved and preferably contained in one solution. The presence of undissolved solids in the sample solution may give low results if the solids contain radium, since they will not release radon at the temperature used for de-emanation. Although small amounts of solids, e.g., silica, may be tolerated, the residue resulting from a particular dissolution treatment must be tested for radium content separately by dissolving and analyzing before the treatment can be used to give reliable results. Naturally occurring materials, such as ores, are usually treated with the conventional acids to dissolve the bulk of the

material and any insoluble residue fused with sodium carbonate. Ashed cadavers have been brought into solution by a similar procedure.^(lh) Materials containing lead and barium sulfates resulting from uranium ore refining can be obtained in a single solution by reducing the sulfates with zinc.^(lf) Urine and fecal samples can usually be dissolved with acids after first destroying the organic matter. Perchloric acid should be used in place of sulfuric acid, since insoluble sulfates which carry radium may be formed when the latter acid is used. Solid samples have also been directly analyzed without dissolution by collecting the radon released during fusion.^(le)

The radon is removed from the solution in a simple vacuum line. A typical line consists of a sample flask arranged so that gas can be bubbled through the solution while it is heated, followed by a water condenser, a gas purification system, counting chamber, and a mechanical vacuum pump. The gas purification system varies with the requirements of the counting system and may consist of heated copper if it is necessary to remove oxygen, a cold trap to remove water and other condensable vapors, and drying agents. Sodium hydroxide is useful for removing acid vapors, and other reagents may be necessary. The sample solution is placed in the flask and the radon removed by boiling for about 15-20 minutes while a stream of gas is passed through the solution, and exhausted through the vacuum pump. Nitrogen, argon, helium, or air may be used. The time at which boiling ceases is noted, the flask sealed, preferably at atmospheric pressure to prevent leakage, and the solution allowed to accumulate radon for a period of time depending on the amount of radium present and the

counting accuracy desired. Radon grows in with a half-life of 3.825 days, and so the growth is 99 per cent complete in about four weeks, and periods of growth ranging from days to full growth are used. If the radon is allowed to reach equilibrium, 1 μg of radium will produce 6.66 disintegrations per minute of alpha activity, due to Rn, RaA, and RaC'. After the growth period, the line is evacuated up to the sample flask. The sample flask is then opened to the line, and the solution boiled for 15-20 minutes while the counting gas is passed through the solution and into the chamber. The radon is thus transferred to the counting chamber in a short period of time compared to the half-life of radon. In low-level work when large volumes of carrier gas are necessary for the transfer of radon, such as when de-emanating large volumes of solution, the radon may be concentrated to permit the use of smaller chambers to obtain smaller backgrounds. Liquid nitrogen ⁽²⁾ and liquid oxygen ^(1b) have been used to condense radon out of the carrier gas. The condensed radon can then be transferred to the counting chamber by sweeping with the counting gas. Adsorption on charcoal has also been used to remove radon from a gas stream. ⁽³⁾ The radon is removed from the charcoal by heating and transferred to the counting chamber. When using charcoal to concentrate small quantities of radon, a correction must be made for the radon derived from the charcoal, or the charcoal must be de-emanated prior to use. One type of charcoal ^(3b) was found to contain 0.013 μg Ra per gram. By using a minimum amount of charcoal, of the order of several grams, this correction may be kept small.

Many counting systems have been used for the actual radon measurement. An early method, still sometimes used, consists of measuring the total ion

current produced in the gas due to the radon and its daughters by a sensitive electrometer. For low-level work, twin-ionization chambers have been used to compensate for cosmic ray background. The disadvantages of this system have been discussed by Curtiss and Davis.^(1c) A more satisfactory measuring system consists of amplifying and counting the individual alpha pulses produced in the chamber, either by operating the chamber in the proportional region and using a pure, free-electron gas, or by operating at lower voltages in the ionization region and collecting either the slow pulses due to positive ions or the fast negative pulses due to electrons. After sufficient amplification, the pulses are sent through a scaling circuit and recorded. Whatever the counting system, the chambers used consist essentially of a metal cylinder of 1-4 liter capacity with a collecting electrode inserted along the axis of the cylinder and insulated from it. In pulse-ionization counting, the diameter of the collecting electrode may be quite large, about 1/16" to 1/2". For proportional counting, the collecting electrode is quite thin, about 0.005" in diameter, to permit operation at reasonable voltages.

Counting the slow positive pulses in an ionization chamber has the advantages that low collecting voltages (several hundred volts) may be used, and the choice and purity of the counting gas is not critical. A low-frequency amplifier is necessary, and this may make the system microphonic and subject to A.C. pickup. The slowness of such a counting system limits its use to low level work only.

When counting the fast negative pulses due to electrons in an ionization chamber, the collecting electrode is made positive, and a free-electron gas such as argon, helium, or nitrogen must be used. To take advantage of the fast pulses produced in such a system, the counting gas must be purified to remove traces of electron-attaching gases, such as oxygen and water vapor. Small amounts of impurities may be tolerated, but the plateau will suffer. The voltages required for such counting varies from 500 to 2,000 volts. For proportional counting, a highly purified, free-electron gas and a high frequency amplifier are usually used. Higher voltages and fine wire collecting electrodes are necessary to obtain sufficiently high electric fields for gas amplification. In order to bring the operating voltage down to about 1,000 volts, pressures lower than atmospheric may be used. Helium permits operation at lower voltages than nitrogen or argon. With negative pulse-ionization counting, high-frequency amplifiers that are relatively insensitive to low-frequency mechanical and microphonic disturbances may be used. Greatest freedom from spurious counts is obtainable with proportional counters.

All the types of counting described have been used successfully for the determination of micromicrogram amounts of radon with good precision and accuracy, and in setting up a new low-level system one may choose from a variety of emanation lines, counting systems, and counting gases.

No matter what counting system is used, the method of calculating the result is identical. The radon is separated and transferred to the counting system in a very pure radiochemical state, and in the chamber, radon decays according to the scheme given in Table I. The alpha activity,

initially due to radon alone, increases with time, reaches a maximum in several hours, and then decays with the half-life of radon. The observed alpha counting rate is a function of the disintegration rates of the members of the radon chain and the counting efficiencies of the alpha emitters. It is expected that radon remains as a neutral atom in the gas phase, and that nearly all its alpha particles will produce sufficient ionization in the chamber gas to be counted, while the solid-element nuclides, being positively charged, will collect on the negative electrode. In the latter case the counting efficiency will be about 0.5, since only about one-half of the alpha particles are emitted in a direction to travel through the gas. The observed counting rate is then given by the equation:

$$A(t) = E \cdot Y_r + (A + C)Y_s, \quad (1)$$

where $A(t)$ is the observed alpha counting rate at time t after separation of radon; E , A , and C are the disintegration rates of Rn , RaA , and RaC , respectively, at time t ; and Y_r and Y_s are the counting yields of Rn and the solid elements, respectively. E , A , and C , as a function of time can be obtained from the familiar Bateman equations for the decay of radioactive chains.

Using these relationships, and under conditions of transient equilibrium, equation (1) becomes:

$$A(t) = e^{-et} \cdot E_0 \left[Y_r + Y_s \frac{a}{a-e} + \left(\frac{abc}{(a-e)(b-e)(c-e)} \right) \right]; \quad t \gg 4 \text{ hours} \quad (2)$$

where e , a , b , and c are the decay constants of Rn , RaA , RaB , and RaC , respectively, and E_0 is the disintegration rate of radon at $t = 0$.

The initial disintegration rate of radon, E_0 , is related to the amount of radium from which it was generated by the equation:

$$E_0 = RS(1 - e^{-e\tau}), \quad (3)$$

where τ is the time of growth of radon, R is the weight of radium, and S is the specific activity of radium.

By combining equations (2) and (3), a relation between counting rate and weight of radium is obtained:

$$R = \frac{A(t)}{e^{-et}(1 - e^{-e\tau})} \cdot \frac{1}{S \left[\frac{Y_r}{Y_s} F \right]} \quad (4)$$

where $F = \frac{a}{a-e} \cdot \frac{abc}{(a-e)(b-e)(c-e)}$. Since Y_r and Y_s are not known, and

there is some question as to the correct value of S , radon counting systems are calibrated by using known amounts of radium obtained by diluting NBS

standard radium solutions. Once the quantity $\left[\frac{1}{S \left(\frac{Y_r}{Y_s} F \right)} \right]$ is evaluated,

the amount of radium can be obtained from the counting rate after applying the proper growth ($e^{-e\tau}$) and decay (e^{-et}) factors. If $Y_s = 0.5$ and

$Y_r = 1.0$, the alpha activity at full growth from 1 μpc of radium will be

about 260 counts per hour four hours after filling the chamber. The various

systems described in the literature give counting efficiencies of about 80

to 90 per cent of the expected maximum rate, or about 230 counts per hour.

To determine micromicrogram or lesser amounts of radium with good accuracy,

it is necessary to have a stable and reproducible counting system with a

low background. Careful selection of materials and cleaning of the count-

ing chamber are necessary to obtain a minimum background. The amount of

radioactive impurities in various metals varies with its composition and

may vary from batch to batch. Stainless steel and copper are usually found to give the lowest backgrounds, while aluminum and brass are usually more contaminated. The chamber should be cleaned before assembly, and the introduction of large amounts of radon into chambers intended for low-level work should be avoided, since the background will gradually increase due to accumulation of Radium F. After use, the radon should be removed from the chamber and the active deposit on the walls allowed to decay before re-use. Since air contains approximately 0.2 μpc Rn/liter, compressed air cylinders, as well as other compressed gases derived from air, should be allowed to age before use to allow the radon to decay, and contamination by room air should be avoided. The electronic system should be stable and free from noise and other non-statistical disturbances.

Assuming that there are no errors in the preparation of the sample for counting and no errors in the operation of the counter, the ultimate error in an analysis is determined by the total number of counts taken. If the standard deviation of a single count is equal to the square root of the total number of counts, then the fractional standard deviation of a radon count is:

$$\sigma_f = \left(\frac{N_s}{t_s} - \frac{N_b}{t_b} \right)^{\frac{1}{2}} / (N_s - N_b) \quad (5)$$

where N_s is the counting rate of sample plus background; N_b is the counting rate of background alone, and t_s and t_b are the appropriate counting times. The backgrounds reported in the literature vary from approximately 15 to 100 counts per hour. With these backgrounds, 1 μg of Ra^{226} , which

will average about 225 counts per hour during the first ten hours, can easily be determined to good statistical accuracy with these backgrounds. It is possible to detect (with a standard deviation of 100%) 0.01 μg Ra^{226} with backgrounds in the lower half of the range given. Table II gives the sample counting times required to count 1 μg of radium to a standard deviation of 5 per cent and the times required to detect 0.01 μg Ra . It appears impractical to detect 0.01 μg Ra when the background approaches 100 cph.

TABLE II

Time Required to Count to a Given Accuracy

Background counts per hour	Time of Sample Count (hr)	
	$\sigma_F = 0.05$ for 1 μg Ra^{226}	$\sigma_F = 1.0$ for 0.01 μg Ra^{226}
15	2.3	6
50	3.0	19
100	3.3	38

Alpha scintillation counting of radon gas has recently been reported⁽⁴⁾ and may prove to be superior to the counting systems previously described. The counting chamber is hemispherical or cylindrical in shape and is fitted with a transparent window. The inner surface is coated with zinc sulfide, which serves as the detector. The radon is transferred to the chamber with a carrier gas and the alpha activity counted by placing the window on the face of a phototube connected to an amplifier, discriminator, and scaler. To obtain good efficiency the chamber must be small, about 100 cc, since alpha particles emitted in the gas phase must reach the zinc sulfide with

sufficient energy to give a light pulse visible to the phototube. For a given chamber size, decreasing the atomic weight of the gas and decreasing the pressure both increase the counting efficiency, since each of these changes increase the range of the alpha particles. Efficiencies of 60 to 75 per cent have been reported. The materials used for chamber construction must be carefully chosen to obtain low backgrounds. Backgrounds of 10 to 20 counts per hour have been obtained with glass chambers, ^(4c) and metal chambers with quartz windows have given backgrounds of 3 counts per hour. ^(4b) An important disadvantage of this system of counting is the restriction on the size of the chamber. This means that small volumes of carrier gas must be used and therefore the sample and transfer line volumes must be kept small, or the radon must be concentrated as described above. However, the simplicity of chamber construction and circuitry, and the low requirements on gas purity together with low backgrounds make the counting system appear attractive.

Separation of radium from other activities and from macro-amounts of inert solids, followed by a measurement of the activity due to radium and its daughters may also be used to determine micromicrogram amounts of radium. Since the chemical operations and the interpretation of counting measurements are considerably more difficult than in the emanation methods, the direct determination of small quantities of radium has not been as widely used or as thoroughly studied as the emanation technique.

Since it is the most commonly encountered problem in the analysis of radium isotopes, let us consider first the determination of Ra^{226} by alpha-particle counting. For accurate counting, the procedure should yield the

radium (plus any carrier) in a form that can be uniformly spread on a counting plate. Since the mounted radium fraction should be as thin as possible, a separation from most of the inactive solids in the original sample is required. It is also necessary to obtain a separation from other radioactive elements, including radium daughters, in order to interpret the counting data correctly. When radium is separated from its daughters, the alpha activity will initially increase at a rate determined by the half-life of radon. For analytical purposes the growth essentially stops at RaD, so the alpha activity contributed by RaF is negligible. If all the radon is retained in the sample, the total alpha activity of the sample, $A(t)$, at any time t after separation is given by

$$A(t) = 1 \frac{1}{3} (1 - e^{-\lambda t}) \quad (6)$$

where λ is the decay constant of radon. A factor of three appears in the second term since radon has two short-lived alpha active daughters. The growth will be essentially complete in about 30 days, and the total alpha activity will be four times the radium activity. In practice, when radium is spread on a plate in a very thin film and counted, some loss of radon occurs due to diffusion and recoil. Since the amount of radon lost is quite variable and depends on the physical characteristics of the mount, it must be determined empirically and corrections made if the losses are significant.⁽⁵⁾ The amount lost by diffusion is quite small, about 2 per cent, even from essentially weightless mounts. However, loss of radon by recoil is significant from thin mounts, and the error introduced by neglecting this loss increases with time as the fraction of activity due to radium daughters increases. The loss by recoil from samples of appreciable

thickness is small and amounts to no more than a few per cent from sample thicknesses obtained when carriers are used. The loss by recoil of other alpha-active daughters need not be considered since the recoil atoms are positively charged and will be collected on the sample if it is the negative electrode in the counter.

The preparation of a sample for a chemical radium separation is similar to that used for the emanation analysis. The sample must be completely in solution or any insoluble material must be checked for radium activity. The separation of radium from large amounts of inactive solids and from other activities is usually accomplished by co-precipitation with carriers, although adsorption of radium on cation-exchange resins has also been used.⁽⁶⁾ The choice of carriers used to carry radium depends on the similarity in crystal structure between salts of radium and some of the other alkaline earth elements, particularly barium, and some of the Pb(II) salts. Lead sulfate and barium chloride are the carriers most commonly used. Lead and barium chromates, barium sulfate, and calcium carbonate and phosphate have also been used. Other carriers are doubtless available. Barium sulfate is useful only as a preliminary step to effect separation from large amounts of solids, since it does not give a clean radio-chemical separation.

A procedure^(6,7) that has been studied in some detail consists of a preliminary precipitation of $PbSO_4$ from dilute nitric acid solution, dissolution of the sulfate in concentrated hydrochloric acid, and a final precipitation of barium chloride from a solution of ether and hydrochloric acid to decrease the solubility of barium chloride. To obtain a uniform

sample mount for accurate alpha-particle counting, the barium chloride is dissolved in water, transferred to a counting plate, and barium sulfate precipitated by adding a few drops of dilute sulfuric acid. Before adding the sulfuric acid, the barium chloride solution should be heated for several minutes to drive off any radon that has accumulated since the barium chloride precipitation. The barium chloride precipitation effects a separation of radium from its daughters. The amount of RaA, B, and C in the mounted sample that is unsupported by the radon parent is proportional to the length of time between the barium chloride precipitation and the radon expulsion on the plate. After the radon removal, radon and its daughters begin to grow at a calculable rate, while the radon daughters originally present in the sample begin to decay. If the amount of RaA, B, and C initially present is sufficiently great, the counting rate of the sample will decrease for several hours before the radon growth can be seen. It is advisable to keep the time between the barium chloride separation and the radon expulsion short so that the radium sample follows the calculated growth curve as soon as possible after the sample is prepared.

From a count taken at any time after the residual RaA, B, C has decayed to zero (a few hours after radon expulsion), the activity due to radium can be calculated by applying equation (6). To obtain the radium content from the counting rate, it is necessary to know the geometry of the counter, the amount of backscattering and self-absorption, and the radiochemical yield of radium. The backscattering factor is not precisely known, but in the common "50% geometry" counter, a combined geometry and

backscattering factor of 0.515 is within 1 per cent of the correct value, whether glass or platinum is used as the backing material. The recovery and self-absorption factors must be determined empirically by analyzing standard radium solutions under conditions identical to those used in the actual analyses. Recoveries of about 95 per cent are obtainable. For sample thicknesses of about 1 mg/cm^2 , the self-absorption factor is about 0.9.

The combined PbSO_4 - BaCl_2 precipitation gives excellent separation from uranium, thorium, and polonium if the plate is flamed. Less than 0.05 per cent of these elements appear in the final precipitate. Separation from protoactinium and bismuth activities is not quite so good; up to 2 per cent of these elements may appear in the final mount. Actinium is carried to the extent of nearly 10 per cent, and this must be considered if large amounts of actinium or MsTh_2 are present. Difficulty is sometimes encountered in precipitating lead sulfate and carrying the radium from ashed urine or fecal samples or dilute acid solutions that have been concentrated by evaporation. This is most often the result of a high acid concentration. The solution should be about 0.1M in nitric acid for successful precipitation. Large amounts of calcium also interfere, but 5 mg of calcium per milliliter can be tolerated if the lead concentration is 0.5 mg Pb/ml. Difficulty is also sometimes encountered in dissolving the lead sulfate in hydrochloric acid if the precipitate is allowed to stand dry for long periods. To avoid this, the lead sulfate should be dissolved immediately after it is separated. The carrying of radium by barium chloride is best carried out if the barium is added first and followed

by the hydrochloric acid addition. Since in this procedure the barium must be added to an excess of chloride ion, the solution should be thoroughly stirred for several minutes to obtain rapid and complete carrying. The barium concentration must exceed a certain minimum value for complete carrying. Four milligrams of barium has been found sufficient for a final volume of 10 ml of ether-hydrochloric acid solution.

This procedure will not, of course, distinguish between radium nuclides. If the presence of more than one radium nuclide is suspected, the separated radium should be counted at various times after separation, and the change in activity compared with those calculated for the various radium nuclides. The growth of alpha activity into Ra^{226} with a 3.825d half-life has already been discussed. The radium isotope in actinium series, Ra^{223} (AcX), is followed by relatively short-lived descendents, including three alpha-emitting nuclides. Shortly after separation, this chain will decay with a half-life essentially that of Ra^{223} , 11.2 days, and the total alpha activity will be four times as great as the Ra^{223} activity. Ra^{224} (ThX) has two immediate short-lived alpha-emitting daughters that complete their growth in a few minutes. Another alpha-active daughter (ThC) grows in more slowly, so the total alpha activity of pure ThX rapidly grows to three times the activity of ThX, passes through a broad maximum, and begins to decay, finally reaching transient equilibrium with a 3.64d half-life. Thus, from the variation of alpha activity with time, the composition of a mixture of these nuclides can be calculated. Concentrations of Ra^{226} and ThX in water have been determined in this way. (8) Ra^{228} (MsTh₁) can be determined by alpha particle counting

if it has aged a sufficient length of time to contain appreciable quantities of 1.9y Th^{228} (RdTh). In this case the RdTh or its daughter (ThX) can be separated and counted. If the amount of RdTh growth is not known, or is insufficient, the beta activity of the first descendent of MsTh_1 , 6.1h Ac^{228} (MsTh_2) may be counted, either as it grows into pure MsTh_1 or as it decays following separation. Thenoyltrifluoroacetone has been used to separate Ac^{228} for this analysis. (9)

Separation procedures using carriers other than the one described can be devised, and adsorption on ion-exchange resins can be used analytically to separate radium from many elements. Thenoyltrifluoroacetone can be used to extract polonium, bismuth, and lead from radium by proper adjustment of the acidity, (10) and this step, preceded by a lead sulfate precipitation, might be used to obtain relatively carrier-free radium for counting. Separation of radium from its daughters has also been achieved by both paper chromatography and electrochromatography, and this type of separation could receive analytical application. (11)

Gamma ray counting of micromicrogram amounts of radium appears to have no advantage over alpha counting, although for bio-assay work gamma scintillation counting of radium in the body would be very successful if time and equipment were available. As little as 0.001 microgram of radium in the body can be detected by in vivo measurement, and amounts greater than 0.03 microgram can be readily determined. (12)

The sensitivity of the co-precipitation method is about equal to that of the radon emanation method. Alpha counter backgrounds of 2 to 3 counts per hour can be readily obtained if chamber materials are carefully selected.

The reagents may produce another three counts per hour. The over-all counting yield is about 40 per cent, so that 1 μg of radium will produce about 210 counts per hour at full growth. This is to be compared with a maximum counting yield of about 230 counts per hour and minimum backgrounds of about 3 to 15 counts per hour for the emanation method. The precipitation procedure, however, suffers in accuracy when compared to the emanation method. Thick samples are difficult to count accurately, even though corrections are made, since there may be differences in uniformity of spread between samples. Some contamination by other nuclides is always possible. The radiochemical yield may be variable since it depends on many factors, such as the composition of the sample, temperature of precipitation, amount of stirring, etc. There are more opportunities for errors to occur than in the emanation procedure. The excellent selectivity of the emanation method is an advantage when only Ra^{226} is desired; however, separation and counting of radium is necessary when other radium isotopes are to be detected. The emanation procedure, however, is more difficult to set up and perform, requires special equipment, and is more time-consuming. The emanation procedure has one advantage which cannot be overcome by any radium separation procedure. It is an excellent example of non-destructive testing, since the same sample can be analyzed any number of times. Thus, each method has an area of application where it is the preferred or required procedure.

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COUNTING TECHNIQUES AND INSTRUMENTATION

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The Analytical Chemistry section of our Analytical Laboratory Department is called upon frequently to analyze air dust, water, and other miscellaneous samples for alpha and beta activity. This paper will be divided into two parts, the first part will describe the techniques employed in the analyses, and the second part will summarize an instrument evaluation made by Mr. Frank Carr of our Instrument section.

COUNTING TECHNIQUES

Air Dust: In taking air dust samples, our Industrial Hygiene Department uses the Hudson Pump, or Gast Pump, modified to accommodate a 1-1/8" diameter Whatman No. 41 filter paper. There are two general types of alpha air dust samples taken--uranium and thorium. The uranium samples are counted after four or five hours have elapsed--to allow for the decay of radon gas, and the thorium samples are counted after approximately 24 hours have elapsed--to allow for the decay of thoron and other short-life daughter products.

The air dust samples are generally counted in alpha scintillation counters. The background and the geometry of the counters are taken daily, before any samples are counted. The normal background runs around 0.2 c/m and the geometry is approximately 42 per cent. The sample is placed on the pedestal of the counter and fastened down with a plastic ring. The sample is then pushed into place and raised into the counting

position. Each sample is counted for 32 counts, or for 15 minutes, whichever comes first. If a 32 count is reached in only a few seconds, the sample is counted again for longer count rates.

After the count has been taken, the results are reported in $d/m/m^3$ knowing the rate of flow through the Hudson Pump, geometry, background, count rate, and using a 30 per cent factor for absorption with Whatman No. 41 filter paper. The use of a 30 per cent absorption factor has been reported by John Alercio and John Harley.⁽¹⁾ In studies made at National Lead, we have found that a 30 per cent absorption factor is a good average figure to use if a correction is to be made for absorption.

We use as an air dust tolerance $70 d/m/m^3$ and we have found that when our uranium air dust levels go above this amount, our uranium urine results tend to go above the 0.05 mg U/l tolerance.

Water Samples: "Clear Water" samples are plated directly onto a stainless steel counting planchet, two inches in diameter, in the following manner:

The water sample is shaken well, and a 20-ml aliquot of the sample is plated onto a stainless steel planchet and dried on a medium-heat hot plate. (The background of the planchet and the geometry of the counter are taken prior to the plating.) After the aliquot is dry, the planchet is placed on the pedestal of the alpha gas flow proportional counter, (all gas flow counters used in the laboratory operate on argon gas) and then is moved into the counting position. The sample is counted for 15 minutes. The result of the count is then calculated in terms of $d/m/ml$.

"Murky water" samples are analyzed in the following manner: An aliquot of from 20 to 100 ml of sample is placed in a beaker. The same

amount of nitric acid is added to the aliquot and then the beaker is placed on a medium-heat hot plate until about 5 to 10 ml of the mixture remains. The solution is allowed to cool and then about 25 ml more of nitric acid is added and the beaker is returned to the hot plate and kept there until approximately 5 to 10 ml of the solution remains. The solution is allowed to cool and the same procedure is continued until the solution becomes clear. (The nitric acid is used to take care of the organic material as well as insoluble inorganic compounds that are present in the sample.) The remaining aliquot is then plated on a stainless steel counting planchet and allowed to dry thoroughly on a medium-heat hot plate. The sample is then counted in the alpha proportional counter for 15 minutes. The result is calculated in terms of d/m/ml.

The proportional counter has a background of approximately 0.2 c/m and a geometry of about 50 per cent.

One of the primary problems associated with plated alpha activity samples of any kind is the great probability of self-absorption. We try to minimize this possibility by plating as thin a layer as we can on each planchet.

The total alpha activity results are used as comparative indications of trends by the Industrial Hygiene and Radiation Department.

Solid Samples:

Solid samples are plated on stainless steel counting planchets in the following manner:

The weight of the stainless steel planchet is recorded before the aliquot of the sample is deposited on the planchet. After a small

amount of the sample is thinly spread over the surface of the planchet and dried, the planchet is weighed again. The difference is recorded, and after the sample is counted in the gas flow alpha proportional counter for 15 minutes -- the result is calculated in d/m/g.

Here again, one must take into consideration the factor of self-absorption, and care must be employed in preparing a very thin layer of the material on the stainless steel counting planchet. If too thick a sample is counted, the resulting count will only be a surface activity count and not a true indication of the entire sample.

Beta Counting:

Samples counted for beta activity are always prepared as solids. Some examples of the type of samples counted for beta activity are: ashed gum-paper, mud, ashed urine, dried process sludge, filter paper, ashed pleated filters, metal oxides.

Before any samples are counted, the background and the geometry of the beta counters are taken. The end window G.M. beta counter has an average background of eight counts per minute and a geometry of about 4 per cent. The banjo type G.M. beta counter has a background of approximately six counts per minute, and a geometry of about 5.5 per cent. Higher geometries could be obtained by placing the sample closer to the tube, but we use the first shelf of the counters for placing our aluminum absorbers. All sources and samples counted in the beta counters are counted with a 6.51 mg/cm^2 aluminum absorber to remove the low-energy beta rays and the alpha particles.

Beta samples are deposited on a cupped stainless steel counting

planchet -- 1 inch in diameter -- and counted in either of the two beta counters for 3 to 30 minutes, depending on the amount of activity present. The result of the count is either given as d/m/sample, or d/m/g.

When the beta energy of a particular sample is desired, a series of three-minute counts are made using aluminum absorbers ranging from 0.00 mg/cm² to 1616 mg/cm². The fraction of initial activity ($\frac{A}{A_0}$) is plotted against mg/cm² of aluminum on 3-cycle semi-log paper. The beta activity is then interpolated from a beta particle range energy curve.

Instrumentation:

Several of the other A.E.C. laboratories and contractors have constructed their own counting instruments according to their needs. However, National Lead has neither personnel nor facilities to do the design and fabrication. We have found that the use of commercially available instrumentation fulfills our needs adequately.

The instruments for alpha counting presently in use by our Analytical Chemistry Section for analysis of the previously mentioned samples are:

1. The NYOO alpha scintillation counter, Type B-1-11, employing the RCA 5819 photomultiplier tube, with a concave faced light pipe coated with stop-cock grease and a layer of Patterson Type D Zinc Sulphide (silver-activated) of approximately a one grain thickness. This instrument is fully described in NYO-1523 by Graveson, DiGiovanni, and LeVine, 1950.
2. The Nuclear Instrument and Chemical Corporation of Chicago, automatic alpha proportional counting system, using argon as the counting gas.
3. The Nuclear Measurements Corporation of Indianapolis, Model PC-2A

low-background alpha proportional counter, using argon as the counting gas.

Alpha Counters:

Originally, National Lead was under the NYOO Instrument Recall Program, and we were supplied with the instruments they desired us to have. We have found, many times over, advantages in using their alpha scintillation counter. Scintillation counting is a vast improvement over parallel plate counting. The parallel plate chamber is quite unstable, is subject to interference by microphonics, and has a high spurious counting rate. On the other hand, scintillation counters are very insensitive to electrical and acoustical noise, have a low resolution loss, low background, comparatively high geometry and can be provided with sharply defined lines of discrimination to other than the desired type of counting. "The thin coat of phosphor is used so that its conversion efficiency for beta and gamma radiation is very much less than that for an alpha particle."⁽²⁾ As long as a dust-free, fairly constant, not-too-warm room temperature is maintained, the scintillation counter will give trouble-free service and reproducible results. Care must be taken with air dust samples where the particles on the filter paper tend to be loose. Although there is no air or gas motion within the chamber as with a gas flow counter, decontamination and recoating of the tube face of an alpha chamber such as this requires at least an hour under ideal conditions. Should contamination of a nature not removable with detergents and/or solvents be present, a method of electro-polishing is described in the paper prepared by the NYOO.⁽³⁾

In order to obtain speedy results for the Industrial Hygiene and Radiation Department (when large numbers of air dust samples are submitted for analysis, as in complete plant surveys), we use the Nuclear-Chicago automatic alpha proportional gas flow counting system. This unit can be loaded with 35 samples (and can be modified to handle more), can be adjusted to a desired total number of counts from 20 to 25,600, and will automatically count and record the time for each sample up to 999.99 minutes. We use a specially selected Model D-47 gas flow counter with commercial argon counting gas as the detector. This unit is versatile, in that it can be converted to use as an automatic beta counter if desired. Once loaded, it needs no attention and thus releases a technician for other work. It is also used to count samples over night with the additional features of recycling the samples and recounting them an indefinite number of times. By using recycling time, averages can be obtained from the printed tape for each sample to give greater accuracy in counting. The instrument has a background of less than eight counts per hour, and a geometry of approximately 46 per cent. It is easily decontaminated in about one-half hour using Radiacwash and alcohol. Its chief disadvantages are: (1) The D-47 counter has delicate and intricate construction features that require great care in handling during decontamination. (2) In the event of loose dust air dust samples, the background might increase during the counting of a group of samples. (We have not experienced this as yet and hope to avoid it by carefully screening samples in a scintillation counter prior to placing them in the device.)

Proportional gas flow alpha counters have been found to be better suited for counting plated samples than air dust samples. The NMC PC-2A is used primarily for samples such as water, mud, solid, and similar types that would require plating. Due to the chamber construction, a full 2π (50%) geometry can be consistently attained. Backgrounds as low as one count in 12 hours are possible, but usually backgrounds of less than two counts per hour are experienced. The PC-2A uses commercial argon for counting alphas. A solenoid valve is so arranged in the gas flow system that it meters argon gas at an adjustable slow rate to maintain a slight positive pressure in the chamber for counting and also a fast rate for rapid flushing. The rapid flushing tends to eliminate chamber contamination by radon and thoron, but on a few occasions we have experienced the condensing of thoron on the walls of the chamber and, during its decay, a high background counting rate. This high rate falls off to nondetectable levels in a matter of four hours and the instrument returns to normal. The main advantages of the PC-2A have been noted by us to be: (1) Its compact "all-in-one" construction, (2) the ability to use a readily available counting gas, (3) the high geometry, (4) ease of use, and (5) the small amount of time necessary to reduce background due to contamination within the chamber. Decontamination of the chamber can be accomplished in as short a time as ten minutes under ideal conditions, but 25 to 30 minutes are required where major decontamination is indicated. It would be wise to have a complete chamber and pedestal cover (whose operating voltage is known) ready for immediate substitution in the event of a spill of material in the chamber or where other laboratory accidents can occur.

A complete change can be made very easily in less than five minutes. Use of this instrument has proved highly profitable in saving time in some of our analyses for alpha activity.

Beta Counting:

The instruments we use for beta counting are: (1) The Anton Electronics Company, Type 1007, Banjo Type G-M Tube in an El-Tronics Lead Shield and Manual Sample Changer, coupled to a Nuclear of Chicago Model 183 Scaler. A Model T-1 Timer is used when a preset time period is desired. (2) Nuclear of Chicago's Type D-34 G-M tube in their Model 3031B Lead Shield and Manual Sample Changer coupled to a Model 161A Scaler. A T-1 Timer is also used here.

National Lead's present beta-counting instrumentation seems to be sufficient to cover the types of samples we wish to count. G-M type beta counters do not have any particular advantage over a proportional type beta counter except possibly lower voltages being required to operate them. G-M types have no power of discrimination between pulse sizes, as have proportional types, and the G-M tubes have of course a limited life. By use of absorbers of various materials such as brass, aluminum, lead, etc., pulse size or energy discrimination can be accomplished. We have obtained geometry's of from 3.4 to 5.7 per cent, which are low in comparison with those of proportional counters, and backgrounds of 5 to 9.5 c/m, but a rather large advantage G-M type instruments have is in the preparation of samples for which energy curves are desired. Since on the G-M type instruments there is no gas flow, samples of fine particulate matter can be counted without fear of gross contamination. G-M tubes themselves

could not be decontaminated internally, but surface dust contamination can be removed by using a camel's hair brush and a stream of dry clean air.

One particular disadvantage in obtaining the Anton G-M tube and El-Tronics shield combination is that there is no known commercial source for any kind of absorbers. A lot of time and effort, however, produced a set of our own manufacture which have proved to be useful and versatile.

In conclusion, it is pointed out that we have had a great deal of success with all of our commercially available counting equipment; however, it is suggested that anyone desiring to complement their laboratory instrumentation investigate several sources of supply before making a purchase.

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