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Chemistry
(TID-4500, 11th ed)

General Electric Company
KNOLLS ATOMIC POWER LABORATORY
Schenectady, New York

SELECTED METHODS OF CHEMICAL ANALYSIS
FOR THOREX PROCESS CONTROL

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September 1, 1956

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Authorized Classifier

Jan 21, 1957
Date

Operated for the
United States Atomic Energy Commission
by the
General Electric Company
Contract No. W-31-109 Eng-52

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ACKNOWLEDGMENT

The help of many whose work contributed toward the publishing of this manual is fully acknowledged. In particular, the authors wish to thank Merle E. Jones, David J. Fisher, and Mrs. Helen Carach Hendrickson.

ABSTRACT

Step-by-step procedures for control of the Thorex process miniature pilot plant at KAPL are given for use as a laboratory manual. Included are procedures for measuring acidity, density, thorium content, radiation (α , β , and γ), U-233 and U-232. General radiochemical procedures are given for determination of Ce-144, Cs-137, Pa-233, Ru-106, Sn-89, Th-234, total rare earths (TRE) and Zr-95 + Nb-95. Miscellaneous determinations cover n-butanol, dibutyl phosphate (DBP), fluoride ion, fluorimetric uranium, manganese dioxide, manganese, phosphate, tributylphosphate (TBP), and unstable constituents in TBP diluent.

Also included are several methods possibly applicable to determination of free acidity, and analysis of aluminum-thorium mixtures and (MBP-DBP) mixtures. Problems still needing analytical attention are listed as well as a few laboratory techniques.

SELECTED METHODS OF CHEMICAL ANALYSIS
FOR THOREX PROCESS CONTROL

W. W. Sabol and B. F. Rider

INTRODUCTION

The methods contained in this report are those currently in use for analytical control of the Thorex process at the Knolls Atomic Power Laboratory.

Many of the methods have been adapted from earlier versions used in the Redox and Purex process control and have appeared in previous KAPL reports. Methods are selected principally for brevity, simplicity, and adaptability to routine of a control laboratory.

DETERMINATION OF NITRIC ACID

Titration to Methyl Red End Point

Principle of Method

Nitric acid (HNO_3) in aqueous or organic streams can be titrated with standard sodium hydroxide to the methyl red end point ($\text{pH} = 4.6$). Only cold feed solutions, end streams, and interstage samples containing little or no thorium or aluminum ($< 10^{-3} \text{ M}$) can be titrated directly by this method.

Reagents

1. 0.2% methyl red indicator. Dissolve 1.0 g methyl red in 300 ml methanol and dilute to 500 ml with distilled water.
2. 0.1 M NaOH. Standardize periodically against 100 λ of constant boiling HCl.

Procedure

1. Add sample (0.3 to 0.5 milliequivalent) to 10 ml distilled water in an Erlenmeyer flask.
2. Add 2 drops methylred indicator to aqueous solutions. When organic samples are taken, add 4 drops of methyl red to compensate for that portion of the indicator extracted into the organic phase.
3. Titrate with standard NaOH to first yellow tinge in the aqueous layer.
4. Calculate the acidity:

$$\text{M HNO}_3 = \frac{\text{ml NaOH} \times \text{M NaOH}}{\text{ml sample}}$$

Potassium Oxalate Method

Principle of Method

For the determination of acidity in solutions containing thorium and/or aluminum, potassium oxalate is used as a complexing agent. Titration of the free acid to the bromthymol blue end point is accomplished with standard 0.1 M sodium hydroxide. The amount of water used in the procedure is critical. Too much water establishes a buffering action between the oxalate salt and the free acid present which shortens the end point break; the end point is then moved to a lower pH than the indicator change (6.0 to 7.6); the end points become indistinct. A typical titration curve appears in KAPL report 1159.(1)

Reagents

1. 0.05% solution bromthymol blue indicator. To 0.10 g bromthymol blue add 3.2 ml 0.05 M NaOH and dilute to 200 ml with distilled water.
2. 0.1 M NaOH. Standardize against 100 λ of constant boiling HCl with methyl red indicator.

Procedure

1. In a 50 ml Erlenmeyer flask add in the following order:
 - 1 ml distilled water
 - Up to 1.0 ml sample (see Table 1)
 - 3 ml 25% potassium oxalate
 - 3 drops bromthymol blue indicator
2. Titrate with 0.1 M NaOH to the first blue tinge. A green color indicates the approach to the end point.
3. Calculate the acidity:

$$\underline{M} \text{ HNO}_3 = \frac{\text{ml titration} \times \underline{M} \text{ NaOH}}{\text{ml sample}}$$

Suggested Sample Sizes

<u>Expected Acidity, M</u>	<u>Sample Size</u>
0.10 - 0.50	1 ml
0.4 - 0.2	250 λ
1.0 - 4.0	100 λ
> 4.0	25 λ

pH Method

Principle of Method

The pH of a near neutral solution of aluminum nitrate or of thorium nitrate is a sensitive indication of its free acid content.^(1,2) Thus, a measurement of pH can form the basis of a free acid determination if the solution contains only one appreciably hydrolyzed constituent and the concentration of this constituent is known. Reference is then made to standard curves of pH vs free acid molarity at varied salt concentrations.

If samples are acidic or basic they are neutralized with appropriate standard acid or base to 0.00 ± 0.10 M before pH measurement. Limited amounts of other constituents such as sodium nitrate exert only a negligible effect on the pH in the working region (pH = 0.0 to 2.4).

This procedure has been adapted for use on a micro scale where hot solutions containing only thorium are encountered. Remote equipment and microelectrodes are used.

Apparatus and Reagents

1. Beckman Model H-2 pH Meter connected to a Sola constant-voltage transformer.
2. Glass - calomel electrodes.
3. Buffers: pH 7.00, 2.00, 1.40.
4. Standardized HNO_3 and NaOH solutions: 0.05 to 0.50 M, in 0.05-M increments.

Procedure

A. Standardization of Meter

1. Place the electrodes in a small beaker containing pH 7.00 buffer. Wait several minutes for equilibrium and adjust the standardization control to a meter reading of 7.00.
2. Rinse the electrodes with distilled water, dry, and place in a small beaker containing pH 2.00 buffer. Wait several minutes for equilibrium and adjust the meter with the temperature control to a reading of 2.00.
3. Rinse and dry electrodes and place in pH 1.40 buffer before measuring each sample to verify standardization.

B. Direct pH Measurement Technique (Aqueous Samples)

1. Standardize pH meter.
2. Rinse, dry, and immerse the electrodes in the sample. After equilibrium is reached, read the pH meter to the nearest hundredth unit.

3. Refer to Figure 1, "The pH of Aluminum Nitrate and Thorium Nitrate Solutions," and from the known thorium or aluminum content of the sample (obtained by the Density Method, page 9) and the measured pH, obtain the free acidity of the sample.
4. If the resultant $\underline{M} \text{ HNO}_3$ is not within $0.00 \pm 0.03 \underline{M}$, use the neutralization technique, as follows.

C. Neutralization Technique (Aqueous Samples)

1. Standardize pH meter.
2. Mix 1 vol of the sample with 1 vol of standard acid or base that will neutralize the free acidity. The free acidity may be qualitatively known or may be estimated by the direct measurement technique.
3. Rinse, dry, and immerse the electrodes in the sample. After equilibrium is reached, read the meter to the nearest hundredth unit.
4. Refer to appropriate family of curves (Figure 1). The known thorium or aluminum content of the sample (obtained from the density equation, p. 9) is divided in half, since a 1 to 1 dilution with standard acid or base was made on the original sample. Record the resultant free acidity obtained from the proper curve.
5. Calculate the free acidity:

$$\underline{M} \text{ HNO}_3 = \frac{(\text{total ml} \times \underline{M} \text{ HNO}_3 \text{ found}) - (\text{ml} \times \underline{M} \text{ HNO}_3 \text{ added})}{\text{ml sample}}$$

Example: The pH of a sample of $1.0 \underline{M} \text{ Th} (\text{NO}_3)_4$ is measured to be 0.50. In reference to Figure 1, this corresponds to a free acidity of $0.10 \underline{M}$. Since the acidity is not within $0.00 \pm 0.03 \underline{M}$, 1.00 ml of the sample is mixed with 1.00 ml of $0.10 \underline{M} \text{ NaOH}$ and the resultant pH is 1.40. When read from the $0.50 \underline{M}$ thorium curve (because of the 1 to 1 dilution), the apparent free acidity is found to be $+ 0.008 \underline{M}$.

By calculation, then:

$$\begin{aligned} \underline{M} \text{ HNO}_3 &= \frac{(2.00 \times 0.008) - 1.00 \times (-0.100*)}{1.00} \\ &= (0.016 + 0.100)/1.00 \\ &= 0.116 \underline{M} \end{aligned}$$

*Basicity is called negative acidity.

Aluminum Nitrate

Thorium Nitrate

FIGURE I THE pH OF ALUMINUM NITRATE AND THORIUM NITRATE SOLUTIONS

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6. For the most accurate work, checks should be run by bracketing each sample. For example, a solution containing -0.22 M HNO_3 should be run twice, once mixed with 1 vol of 0.20 M HNO_3 and a second time mixed with 0.25 M HNO_3 . The two values are reported as checks or are averaged.

D. Dilution Technique for Dissolver Solutions Containing No Aluminum

1. The vessel used for this procedure is a shallow dish of about 1.5 ml capacity (a platinum fluorimeter dish is in use at KAPL). The dish is placed on a rubber stopper mounted on the chuck of a geared-down stirring motor which is turned upside down.
2. The microelectrodes (Figure 3) are immersed in about 300λ of buffer solution and the pH meter is standardized.
3. Rinse, dry, and immerse electrodes in 300λ of distilled water placed in the fluorimeter dish. Add 5λ of sample and turn on the geared-down stirring motor. Mixing is accomplished by the action of the microelectrodes submerged in the dish solution. After equilibrium has been reached, read the pH to the nearest hundredth unit.
4. If the pH reads between 2.00 and 3.00, use the appropriate curves in Figure 2 to read the free acidity. This is determined by dividing the thorium concentration in the original solution (obtained from the density equation, page 9) by the dilution factor.
5. If the pH reads less than 2.00, add 15λ spikes of 0.2 M NaOH until the pH reads between 2.00 and 3.00. If the initial pH is greater than 3.00, add 15λ spikes of 0.20 M HNO_3 . In either case, record the number of λ 's of spike added and the final pH to the nearest hundredth unit.
6. To calculate the free acidity, read the final acidity from the measured pH on the appropriate curve in Figure 2 as determined in Step 4. Then:

$$\text{M HNO}_3 = \frac{(\text{total } \lambda\text{'s} \times \text{final M}) - (\lambda\text{'s spike M spike})}{\lambda \text{ sample}}$$

DETERMINATION OF DENSITY

Falling-Drop Method for Aqueous Solutions

Principle of Method

The density of an aqueous solution can be easily determined by measuring the rate of fall of a drop of the solution through an immiscible organic medium. (3)

Aluminum Nitrate

Thorium Nitrate

FIGURE 2 THE pH OF DILUTE ALUMINUM NITRATE AND THORIUM NITRATE SOLUTIONS

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FIGURE 3

Micro pH Electrode Assembly

- A. Glass Electrode, Beckman Medical Type 290-1
- B. Reference Electrode, Beckman Fiber Type 270
- C. Salt Bridge (KCl)
- D. Rubber Tubing - Connects Parts B and C

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The method is based on Stokes' Law:

$$\text{cm/sec} = 2 \text{ dgr}^2 / 9 \text{ v}$$

which can be resolved into $d = K/\text{sec}$. The term K is a proportionality constant which includes the acceleration of gravity g , the radius of the drop r , and the viscosity v . The difference in density, d , between the aqueous drop and the surrounding immiscible organic medium then can be plotted against $1/\text{time}$, and a straight line obtained with slope K . The value of K can be regulated by the radius of the drop, the length of fall, and the viscosity of the medium. A 12-in. (30-cm) fall length for a 10λ drop has been adopted, and a constant temperature bath is used to maintain constant viscosity.

The organic media have been selected for low water solubility, low vapor pressure, a viscosity to give maximum range consistent with accuracy desired, low cost, and maximum stability against discoloration. The heavy organic medium used is tetrabromoethane (practical), and the light organic medium mineral oil (viscosity 125/135) to which sufficient *m*-xylene (CP) is added to promote miscibility with tetrabromoethane. In mixtures of these solutions, aqueous samples of all densities from 1.0 to 1.9 can be measured in eight tubes. The entire range of viscosity from 1.0 to 1.9 can be covered in a single tube by use of pure mineral oil (viscosity 125/135), but with poor accuracy. Conversely, mixtures of iodobenzene with *m*-xylene having low viscosity require as many as 200 tubes to cover the same range with great accuracy.

The time required for a 10λ drop to fall 12 in. should be 12 to 50 sec. Longer times are inconvenient and do not increase accuracy significantly; falling times faster than 10 sec. are difficult to time, and conformance to Stokes' Law is jeopardized since the drops will deform from truly spherical.

When the specific gravity of an aqueous sample is completely unknown, the sample should be dropped first in a pilot tube containing pure mineral oil which covers the range from 1.0 to 1.9, and a rough estimate obtained. This is especially true in the case of highly radioactive dissolver samples; if an erroneous estimate is made, the drop may be too light for the organic mixture and will float. This presents a nasty removal problem. It is always good practice to try the lightest organic first. Typical calibration curves for the eight tubes A through H are given in Figure 4. These are obtained by plotting $1/\text{time}$ vs the density at 25°C .

Apparatus and Reagents

1. Glass tubes, $3/8$ -in. diam, 20 in. long, with ringed markings 4 in. from the top and bottom of the tube (12-in. fall length). Eight tubes are required to contain the organics.

2. Water bath to hold tubes at constant temperature and provide shielding from active drops. A water-tight bath, 20 in. x 4-1/2 in. x 20 in., has been assembled at KAPL from plexiglas. In the bottom are lead bricks with holes bored at proper distances to accept the tubes. The bricks supply both shielding from the active drops which collect in tube bottoms and a sturdy base for the whole apparatus. Spraying the bricks with "Krylon" or "Dri-film" protects them from corrosion by water.
3. Dropping pipets calibrated for 10 λ drops (Fisher Scientific Company, No. 6-253-5).
4. Pipet Control (Fisher Scientific Company, No. 6-253-5)
5. Stop watch
6. Organic solutions:
 - No. 1 Tetrabromoethane (practical) (Eastman Kodak Company, No. P-240)
 - No. 2 20 vol % m-xylene (Fisher Scientific Company, No. 6-253-50), 80 vol % mineral oil (Fisher Scientific Company, No. 6-253-55)

Dilute carefully to 1 liter the following volumes of Solution No. 1 with Solution No. 2 for the eight tubes:

<u>Tube</u>	<u>ml</u>	<u>Tube</u>	<u>ml</u>
A	42.0	E	256
B	94.0	F	310
C	148	G	364
D	202	H	416

7. Tube calibration solutions, prepared from ZnCl_2 in 2 M HCl. Two should be available for each tube and should be calibrated at 25°C with a pycnometer.

Procedure

1. Place pipet in pipet control and fill to the top mark with the unknown sample. (The pipet is calibrated to deliver two 10 λ samples).
2. Immerse the tip of the pipet 1/4 in. in the organic solution and expel a 10 λ sample.
3. Remove the pipet from the organic solution so the drop will fall. (It is important not to allow the drop at the end of the pipet to touch the glass tube wall, or else the drop will cling to the side.)
4. Measure the time required for the sample to fall the 12 in. between the inscribed lines on the tube.
5. Repeat the procedure and average the drop times.

6. Calculate the reciprocal of the drop time.
7. Read the density at 25°C from the calibration chart shown in Figure 4. The tube is standardized after the unknown is run. A daily calibration is necessary to compensate for any density or viscosity changes which may take place in the organic solution.

NOTE: The densities of highly radioactive samples are obtained in a similar manner in a shielded primary sampling hood under the following conditions. A remote pipettor discharges the sample into special short tubes, 1/2 in. diam x 10 in. long, with calibration marks 6 in. apart. Two 10 λ drops are timed between the 6-in. marks, and the times are added to equal one 12-in. fall for which the calibration curve is provided.

DETERMINATION OF THORIUM

Density Method

Principle of Method

When thorium is the principal contributor to the density of an aqueous solution, the falling-drop method can serve as the basis for an accurate calculation of thorium concentration. Since other constituents (HNO_3 , NaNO_3 , etc.) also contribute to the gross density, the solutions must be analyzed specifically for these constituents and appropriate correction factors applied. This method is applicable for the determination of thorium in dissolver solutions, LAF, and LBT streams.

Apparatus

1. Falling drop density determination equipment (page 9)
2. Pycnometer or hydrometer

Procedure

1. Determine the density of the solution by the falling-drop method or by other means.
2. Analyze separately for free acidity and for other major constituents.*
3. Calculate the thorium from the following equation:

$$\underline{M}_{\text{Th}} = \frac{d_{25} - 1.0012 - 0.032 (\underline{M}_{\text{HNO}_3}) - \text{OMC}^*}{0.389}$$

*a. The factor for other major constituents (OMC) may be calculated from values of their densities at various concentrations found in Lange's Handbook of Chemistry or other such source.

b. The factor 0.032 for HNO_3 is valid only up to 2.0 $\underline{M}$ HNO_3 .

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Thoron Colorimetric Method⁽⁴⁾

Principle of Method

The thorium content of samples in low concentrations can be conveniently determined by measuring the absorptivity of the colored complex formed with Thoron.*

*1 - (O - Arsonophenylazo) - 2 - naphthol - 3, 6 - disulfonic acid. (Preparation given in Reed, Byrd, and Banks, AECD-2565. Commercially available through Fine Organics Inc., 211 East 19th St., New York 3, New York.)

The optical density is read on a Beckman quartz spectrophotometer at 550 m μ on a 1- or 10-cm path length. This procedure is used for determining thorium losses in waste streams (LAW, LCW), and in the thorium-depleted product stream (LCU).

Interferences include zirconium and U⁺⁴ which also form colored complexes that are measured. Cations of lead, barium, calcium, zirconium, aluminum, copper, nickel, sodium, NH₄⁺, and Fe⁺² do not interfere. Fluoride interferes, and the sample should not contain more than 0.05 μ moles fluoride⁽⁵⁾ (50 λ of 1.0 M F⁻), beyond which fuming to dryness with HNO₃ and HClO₄ is necessary. Anions which complex thorium more tightly than "Thoron" interfere, of course, and these should be removed.

Apparatus and Reagents

1. Beckman Model DU Quartz Spectrophotometer, with adapter for 10-cm cells.
2. 1.0- and 10.0-cm cells.
3. Volumetric flasks, 10 ml.
4. HCl, conc.
5. 0.10% aqueous solution of "Thoron".
6. Micropipets and pipet controls.

Procedure - Aqueous Samples

1. Place in a clean 10-ml volumetric flask:
 - 3 to 5 ml distilled water
 - 200 λ concentrated HCl
 - Sample containing 0.2 $\pm$ 0.2 μ mole thorium.
2. Run a blank in a similar manner with each series of determinations.
3. Add 1.0 ml 0.10% Thoron reagent and dilute to the 10-ml mark.
4. Read the optical density in 1.0- or 10.0-cm cells at 550 m μ after setting the instrument to zero optical density with the reagent blank. (Slit setting is about 0.02 mm.)

5. Calculate:

$$\underline{M}_{Th} = \frac{(\text{optical density at } 550 \text{ m}\mu) \times (\text{Factor})}{\lambda \text{ sample}}$$

The factor is determined by running an aliquot of a gravimetrically standardized thorium solution in the manner described above. The linear relationship of optical density at 550 m μ vs μ moles thorium present holds over the range of thorium concentrations in use. A standard is run daily.

Procedure - Organic Samples

1. Place in a clean 15-ml graduated centrifuge cone:

3 to 5 ml distilled water

200 λ HCl, concSample containing 0.2 $\pm$ 0.2 μ mole thorium

2. Mix thoroughly to back-extract the thorium into the aqueous phase.

3. Add 1.0 ml Thoron reagent and dilute aqueous phase to 10-ml mark. Mix.

4. Centrifuge to separate phases, and transfer the bottom layer to the spectrophotometer cell with a transfer pipet.

5. Calculate the thorium content as above.

Suggested Sample Sizes

<u>Thorium, M</u>	<u>Sample Size, 1-1000 dilution</u>	<u>Thorium, M</u>	<u>Sample Size, Direct</u>
0.4 - 2.0	200 λ	4.0 x 10 ⁻³ - 2.0 x 10 ⁻²	20 λ
0.1 - 0.4	1.0 ml	8.0 x 10 ⁻⁴ - 4.0 x 10 ⁻³	100 λ
0.02 - 0.1	4.0 ml	2.0 x 10 ⁻⁴ - 8.0 x 10 ⁻⁴	500 λ
		5.0 x 10 ⁻⁵ - 2.0 x 10 ⁻⁴	2.0 ml
		< 5.0 x 10 ⁻⁵	8.0 ml

RADIATION MEASUREMENTSAlpha Counting

Alpha counts are measured on a methane flow proportional counter by a Borkowski chamber⁽⁶⁾ coupled with a Simpson amplifier (Instrument Development Laboratory Model 117) and are reported at 52% apparent geometry in counts/min/ml of sample. The chambers are purged with methane for a minute prior to each count and the methane is exhausted from the room through a methane exhaust line to which each counter is connected. A 15-min background is recorded each morning and backgrounds should be less than 10 ct/min.

Contaminated chambers may be cleaned with facial tissues moistened with methanol or acetone. Samples are counted for a time sufficient to collect 5000 counts or for 5 min, whichever is shorter.

The alpha counters are standardized daily with a U-233 standard plate. Voltage plateaus are recorded monthly.

To achieve a low operating voltage and to minimize spread error, it is desirable that the central stainless steel wire in the counting chamber be as small as 1/2 mil in diameter. However, for beta tolerance it is best that it be as large as 3 mil in diameter. A compromise of 1 mil is made.

The Borkowski chamber - Simpson amplifier is capable of better beta discrimination than any other proportional counter tested. (7) However, each counter must still be checked for beta interference. In the presence of 10^9 dis/min of beta activity there is about a 225-volt plateau between the alpha threshold and the beta threshold. Each machine is operated in the center of this plateau, at least 100 volts above the alpha threshold and at least 100 volts below the beta threshold.

It should be noted here that Pa-233 is the principal beta interference to alpha counting in short-cooled (70 to 90 day) dissolver solutions. It is further of interest that this isotope is a soft beta and a soft gamma emitter which has been intentionally discriminated against by heavy absorbers on the beta and gamma counters. As a result, no beta ray from Pa-233 enters the beta counters and only a portion of the most energetic gamma (0.315 Mev) enters the gamma counter. The counting efficiency for this gamma is of the order of one or two per cent. Hence, the presence of large quantities of Pa-233 is often forgotten. However, spurious alpha counts on "green" dissolver solutions can be avoided by limiting the amount of Pa-233 mounted on an alpha plate to 10^8 dis/min (which is 10^6 γ ct/min Pa-233 determined by gross gamma scintillation counting). A suitable high beta plate to determine the beta threshold can be prepared by direct mounting 10^9 dis/min Pa-233 (as determined by 4π counting an aliquot of diluted stock). Since such a source has only a 27-day half-life, a substitute source of larger half-life such as Sr-90 would be equally suitable and less hazardous from a gamma radiation point of view.

Because of the potential radiation hazard persons who handle alpha plates with high beta activity should use long shielded tweezers and should wear finger ring monitors.

Coincidence corrections are small and not applied. Adapter rings are available for the chamber for use in conjunction with the 1-in. and 1-1/2-in. lipped dishes commonly used. Flat plates may be placed in the bottom of the chamber with the adapter ring removed or may be placed in the chamber on a 1- or 1-1/2-in. dish.

After mounting, the plates are coated with a thin film of collodion to prevent contamination of the chamber with any loose material on the plate. A film 0.025 mg/cm^2 thick is achieved by applying 3 to 5 drops of collodion (0.5 mg dried collodion per ml of 1-1 ethanol and ether) on a 1-in. plate or 7 to 10 drops on a 1-1/2-in. plate. If collodion is applied only to this recommended thickness, alpha counting efficiency is unaffected.

The pressure in the methane lines to the counters should be kept low-- at about 1 psi on the tank regulator gauge. When no machines are being purged, the rotameter in the line should not show any visible flow ($< 0.1 \text{ cfh}$) although the gas bubbler on each machine should show about 1 bubble/sec. Leaks are present if the rotameter reads $> 0.1 \text{ cfh}$ and no chambers are being purged. Purging at the rate of about $500 \text{ cm}^3/\text{min}$ for 1 min is adequate before the plate is counted. Methane tanks should be replaced with another tank when the pressure falls to 100 psi.

Beta Counting

Beta counts are made with helium-filled GM tubes (Tracerlab TGC-1) with a 25-mg/cm^2 (1/2-mil) gold foil fastened over the tube window in conjunction with a Berkeley two-decade scaler, Model 110A or Model 2105. The use of helium-filled tubes and the gold foil was introduced in controlling the Purex process to discriminate against plutonium X-rays and U-237 soft betas and conversion electrons.⁽⁸⁾ Their continued use in controlling the Thorex process is effective in reducing sensitivity to low energy Pa-233 beta and gamma radiations. Relative decontamination measurements are still valid as long as all beta plates are counted under the same conditions. Without absorbers virtually all beta and gamma counts in dissolver solutions cooled 70 to 90 days would be Pa-233.

Each machine is standardized with a uranium foil standard. Counts are normalized to 10% counting yield for UX_2 . For relative counting efficiencies for isotopes of other energies, see Figure 5. A 15-min. background is recorded daily and chamber background is usually less than 50 ct/min. A voltage plateau is run at least once a month. The operating voltage is normally 75 to 100 volts above counter threshold.

Three shelves are available in the chamber. Any absorbers to be used are placed on the first (top) shelf and samples are placed on the second or third shelf, depending on the amount of beta activity on the plate. When the count is over 10,000 ct/min, the bottom shelf is used. In this case the factor to normalize 10% UX_2 is determined by counting the standard uranium foil in the same position.

A coincidence correction of 1% for each 1000 ct/min is applied to gross counts before corrections for background and geometry are applied. Because of the large coincidence phenomenon encountered with GM counters and the approximate nature of the corrections, no attempt is made to make use of counting rates in excess of 10,000 per min.

Aluminum absorbers are provided and it is important that these be kept free of contamination. They should be checked periodically and cleaned by wiping with acetone or dilute nitric acid.

Gamma Counting.

Gross Gamma Counting

Gamma counts are made on a sodium iodide scintillation counter through 5.2 g/cm² of lead (3/16 in.) and reported as ct/min/ml at 10% efficiency for Cs-137. A scintillation counter is used in preference to an ion chamber because of its greater sensitivity. The absorber is used to give the counter an energy response similar to that of an ion chamber, between 0.3 and 0.8 Mev, with counting rates proportional to dose-rates. Detailed discussions of absorbers in scintillation counting have been published.^(8,9,10)

The operating voltage for the scintillation counter is set 50 volts below the voltage at which the dark current pulses are 1 ct/min; the voltage is determined by placing an opaque metal foil between the photocell and phosphor and taking a 10-min count. The input sensitivity of the scaler should not be changed without determining a new operating voltage.

A daily background for 15 min is taken each morning. The background is normally less than 100 ct/min on the cylindrical crystal (2 in. diam x 1/4 in.). Even though the counter is shielded with 4 in. of lead, samples containing gamma activity should not be stored near the counter since they raise the background. The counter is standardized daily to obtain the factor for a 10% counting efficiency with a standard Cs-137 plate that contains about 30,000 dis/min. This is equivalent to the gamma activity of 1g of natural uranium in an ion chamber.

The standard position for mounts is 1/8 in. from the surface of the source to the face of the lead absorber which is tight against the crystal window. For dish mounts 1/8 in. deep, the lip of the dish is pressed firmly against the absorber which is covered with paper for ease of decontamination. This covering is sometimes necessary even though all plates are covered with cellophane. For filter paper mounts on cardboard, a 1/8-in. spacer ring is used between the sample and absorber.

Samples reading over 35,000 ct/min are counted on the bottom shelf. The normalizing factor to 10% Cs-137 efficiency is obtained by counting the standard plate in the same position. If the count is still greater than 35,000 ct/min, a new mount with a smaller sample size may be prepared. Coincidence corrections are small and are not applied.

Gamma Scintillation Spectrometry

A single-channel scintillation spectrometer is used to good advantage when resolution of one or more gamma emitters from each other is necessary.⁽¹¹⁾ The instrument employed⁽¹²⁾ has a 2-in.-long x 2-in.-diam right cylinder of thallium-activated sodium iodide. A resolution of 7.5 to 9.0% full width at half-peak height for Cs-137 has been obtained, made possible by the installation of a selected photomultiplier tube. Under these conditions the instrument shows a peak-to-valley ratio of 18 to 25 and a photo-to-Compton peak ratio of 4.7 with the crystal in use.⁽¹³⁾ A large crystal is employed in spite of its low resolution (compared with small crystals) because its faster counting rate is useful in reducing counting times. The Atomic Instrument Co. Model 204B linear amplifier is operated at such gain as to place the Cs-137 photopeak at a base line setting of 660 on the pulse analyzer described in ORNL-1470.⁽¹⁴⁾ The window width is operated at a dial setting of 300 (3.0 volts). Figure 6 relates the counting efficiency of gamma emitters of various energies.

The spectrometer has shown good stability over 8-hr periods, constant resolution, and constant Compton scattering-to-photopeak ratios; hence measurements can be made at various photopeaks to obtain a gamma analysis. Certain photopeaks such as those of Zr-95 + Nb-95, Pr-144, and Cs-137 are not completely resolved. Furthermore, Compton scattering from most energetic gamma emitters must be compensated. This is done most conveniently in exacting situations by the solution of simultaneous equations. Spectra of the pure activities in process streams are normalized to unity at their principal photopeaks and appropriate equations set up for the number of photopeaks under consideration. (See page 21)

In routine process control, such exacting situations do not arise frequently. Since there are no gamma emitters of higher energy than Zr-95+ Nb-95 in appreciable amount, the solution of simultaneous equations is unnecessary. Only the contribution of zirconium-niobium Compton scattering is corrected for under the other photopeaks measured.

The scintillation spectrometer is first standardized daily with a Cs-137 standard plate. The window is opened to integrate and the base line is set at 660, corresponding to 660 kev Cs-137 energy. The gain on the linear amplifier is adjusted until a predetermined counting rate is obtained. This is to make the dial read directly in kev. A brief scan across the photopeak is made with a window width of 300 (about 3.0 volts). The counting rates at 680 and 640 should be nearly equal, to show that the 660 count is in the center of the photopeak. A linear feedback amplifier which will accomplish this automatically is under construction.⁽¹⁵⁾

The photopeak maxima for various activities such as Zirconium-niobium, cesium, and ruthenium (distilled from the current slug being run) are determined by scanning across their respective photopeaks. A 5-min background count at the photopeak setting is then taken, followed by a count of the standard plate at the same setting and on the gross gamma counter. A ratio

FIGURE 6.
RELATIONSHIP OF COUNTING EFFICIENCY WITH GAMMA EMITTERS OF
VARIOUS ENERGIES

of the gross gamma count to the spectrometer count gives the factor which relates the scintillation spectrometer measurement to the gross gamma measurements. Typical factors for various fission-product activities are:

Zirconium-niobium	= 10.8
Cesium	= 6.6
Ruthenium	= 4.6
Protactinium	= 0.8

These factors are dependent on individual instrument characteristics, such as the crystal, electronic circuitry, phototube, etc.

Finally, the amount of Zr-Nb-Compton scattering which appears under each of the other photopeaks of interest is established by counting the standard Zr-Nb plate at each of the photopeaks and normalizing to unity at the Zr-Nb photopeak. In this manner, the major corrections can be applied with the least loss of time and accuracy to the counting of activities such as ruthenium and protactinium which have lower gamma energies than Zr-Nb. The final equations for calculating the specific fission-product activities in ct/min take the following form:

$$\text{Zr-Nb} = \text{Zr-Nb Factor} \times \overline{760}$$

$$\text{Cs} = \text{Cs Factor} \left[\overline{660} - \text{Fraction at 660} \times \overline{760} \right]$$

$$\text{Ru} = \text{Ru Factor} \left[\overline{550} - \text{Fraction at 500} \times \overline{760} \right]$$

$$\text{Pa} = \text{Pa Factor} \left[\overline{315} - \text{Fraction at 315} \times \overline{760} \right]$$

where: $\overline{760}$, $\overline{500}$, $\overline{315}$ = Plate counts at Zr-Nb, Ru, Pa photopeak less counter background

Fraction at 660, 500, 315 = Fraction of Zr-Nb photopeak appearing under Cs, Ru, Pa photopeaks.

The standard position of mounts is 1/8 in. from the surface of the source to the canned NaI(Tl) crystal. For dish mounts 1/8 in. deep, the lip of the dish is pressed firmly against the beta absorber which is covered with paper for ease of decontamination. This is sometimes necessary even though all plates are covered with cellophane. For filter paper mounts on cardboard, a 1/8-in. spacer ring is used between the sample and absorber.

Samples counting over 35,000 ct/min are remounted with a smaller sample size. Coincidence corrections are small and are not applied.

The use of the scintillation spectrometer permits some specific fission-product analyses on gross beta-gamma mounts (mainly Zr-Nb) without prior separation of other activities (see Figure 7). It is particularly useful in the separation of two gamma activities which have different energies but are chemically similar, such as Pa-233 and Nb-95, when an adequate radiochemical separation for one of the constituents followed by a gross gamma count would be difficult. A gamma scan of purified thorium product showing the gamma spectrum of the Th-228 chain appears in an earlier report.⁽⁵⁾

General Electric Company, K-1 Atomic Power Laboratory

DETERMINATION OF URANIUM

U-233 by Direct Mount

Principle of Method

Uranium in solutions that are relatively free of foreign salts, or in solutions that may be diluted to a low concentration of foreign salts, may be determined directly by alpha counting. In the absence of absorbing matter on the dish, 1 μg of U-233 will give 1.05×10^4 counts/min at 52% geometry. The method is applicable to LCU streams, when thorium is absent.

A total alpha count of the dissolver solution or of the LAF will include other alpha emitters (U-232 and its decay chain)⁽¹³⁾ as well. Therefore, care must be taken when the results are being analyzed. Extreme caution must be exercised on those plates containing relatively large amounts of protactinium (see page 15).

Apparatus and Reagents

1. Radiant heater
2. Forceps
3. Stainless steel dishes, 1/8 in. deep.
4. Microwash bottle containing 1 M HNO_3 .
5. Paper wipes.
6. Collodion solution, 0.5 mg/ml (0.5 mg dried collodion per milliliter of 1:1 ethanol and ether).

Procedure

1. Rinse a stainless steel dish with acetone and place it on an asbestos square under a radiant heater.
2. With a micropipet, transfer the sample or an aliquot onto the center of the stainless steel dish. Avoid a discharge of air from the pipet into the solution which might spatter the sample.
3. With a microwash bottle or medicine dropper, deposit 2 separate droplets of 1 M HNO_3 onto the dish in such a position they will not readily merge.
4. Rinse the micropipet twice by drawing each of the droplets in and expelling the wash liquid back onto the dish.
5. Slowly evaporate the sample and washes to dryness with the radiant lamp.
6. After the dish is cool, add a sufficient number of drops of collodion to just cover the dish (3 drops for a 1-in. dish, 7 drops for 1-1/2-in. dish). Allow the dish to stand until the collodion solution has evaporated.
7. Count for alpha. Calculations:

$$\text{ct/min/ml U-233} = \frac{\alpha \text{ count/min}}{\text{ml sample}}$$

U-233 by Hexone Extration ⁽¹⁶⁾

Principle of Method

A direct mounting technique is not applicable to solutions which contain a high concentration of foreign salts and a low U-233 content. In this case, an extraction technique is employed to separate the uranium from the foreign salts to prepare a plate suitable for alpha counting.

The sample is discharged into an aqueous phase heavily salted with lithium, ⁽⁷⁾aluminum ^(1,13) or ammonium nitrate which is then contacted with an equal volume of hexone. When the hexone phase is mounted the plate can be alpha-counted accurately. The recovery of U-233 from known solutions is $86 \pm 5\%$. The procedure is used for U-233 alpha determination in LBT streams.

Apparatus and Reagents

1. Extraction vessel with stirrer
2. 4.0 M LiNO₃ or 1.6 M Al(NO₃)₃ neutral (D₂₅ = 1.250, pH = 0.75)
3. Hexone
4. Heating block
5. Stainless steel dishes, 1-1/2 in. in diameter

Procedure

1. Rinse the extraction vessel by filling to the side arm with acetone. Discard the acetone and fill the vessel with water. Repeat with a final acetone rinse.
2. Add 2.0 ml of salting agent to extractor.
3. Discharge 100 λ LBT into the above solution and flush the pipet two or three times to ensure complete transfer of the sample.
4. Stir the solution with the motor-driven stirrer for a few seconds to mix the sample and salt.
5. Add 2.0 ml hexone and stir for 10 min at a rate to intermix the two phases thoroughly.
6. Allow the phases to separate cleanly and then carefully mount 500 λ of the hexone phase on a 1-1/2-in. dish on the heating block.
7. Count for alpha:

$$\text{ct/min/ml U-233} = \frac{\text{counts/min} \times 4}{\text{ml sample}}$$

U-232 in U-233 By Alpha Pulse Analysis

Principle of Method

The importance of U-232 in the Thorex process is discussed in some detail in KAPL-1271.⁽¹⁷⁾ Alpha pulse analysis furnishes a method for determining U-232 product.⁽⁵⁾ The alpha pulses are 5.31 and 4.80 Mev, respectively, and are far enough removed from each other to permit easy peak separation. Since the specific activity of U-232 is over 2000 times that of U-233, alpha analysis is also quite sensitive for the isotope. This analysis is not affected by the presence of Th-232 which complicates mass spectrometer measurements. Beta and gamma activities present in the dissolver solution must be separated since they affect the instrument base line which broadens the resolution of various alpha pulses. U-232 is determined only in purified uranium fractions.

Apparatus

1. Single-channel pulse amplitude analyzer, obtained from ORNL, Model Q970-1. An excellent description of this instrument in use with necessary equipment for obtaining alpha, beta, gamma, and X-ray energy spectra is available.⁽¹⁸⁾
2. Alpha ionization chamber⁽¹⁸⁾

Procedure

1. An alpha plate is prepared by the hexone extraction of uranium from a salted aqueous phase. (See page 24.)
2. Place the plate in the alpha chamber, pump out the air, and flush the chamber twice with P-10 gas (90% argon - 10% methane).
3. On the basis of the alpha activity on the plate, the proper instrument settings (gain, storage circuit, sensitivity, slit width, etc.) are made to give the best spectrum on the attached recorder.
4. After the scan is complete, calculate the fractional distribution of alphas between U-233 at 4.80 Mev and U-232 at 5.31 Mev. Typical scans are given in Figure 8.
5. Multiply the uranium alpha content of the sample, obtained by the conventional alpha counting technique, by the fraction which was obtained in Step 4 to obtain the U-232 content.

$$\text{ct/min/ml U-232} = \text{Total } \alpha \text{ ct/min/ml} \times \frac{\text{U-232}}{\text{U-232} + \text{U-233}}$$

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TYPICAL SPECTRA FOR DETERMINING U-232 IN U-233 BY ALPHA PULSE ANALYSIS

Relative Counting Rate

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KAPL-1147

GENERAL RADIOCHEMICAL PROCEDURESCe-144 by Iodate PrecipitationPrinciple of Method

Cerium ion is held in the +3 valence state during a zirconium iodate precipitation which scavenges the solution of zirconium, niobium, protactinium, and UX. Oxidation of cerium to the +4 state is followed by precipitation as ceric iodate for mounting. After equilibrium is established between Ce-144 and its daughter Pr-144 (2 hr), the sample is counted for betas through a 353-mg/cm² aluminum absorber which absorbs all activity except for a portion of the Pr-144. The beta count obtained is multiplied by an absorber factor (2.9) to correct for the absorbed portion of the Pr-144 activity. Since equilibrium between the two daughters has been established, the Pr-144 count is equivalent to the Ce-144 count. Typical decontamination factors are:

<u>Isotope</u>	<u>Chemical df</u>	<u>Counting df</u>	<u>Total df</u>
Zr-Nb	30	40	1200
Sr	300	2	600
Ru	30	8	240
UX	100	2	200
Pa	70	30	2100

Apparatus and Reagents

1. Glass scoop which will deliver approximately 0.1 g KBrO₃
2. Cerium carrier (10 mg Ce/ml)
3. Zirconium carrier (10 mg Zr/ml)
4. Lanthanum carrier (10 mg La/ml)
5. HNO₃ conc
6. 6% H₂SO₃
7. 0.35 M HIO₃
8. Solid KBrO₃
9. KIO₃ wash solution; 8 g of KIO₃ and 50 ml of concentrated HNO₃, diluted to 1 liter with water
10. 24-mm filter paper (S and S No. 507 or Whatman No. 50)

Procedure

1. Place 10 ml water, 1 ml concentrated HNO₃, and appropriate sample in a 50-ml centrifuge tube.
2. Heat to boiling, and, to destroy any oxalates or peroxides, drop in 0.1 N KMnO₄ until a pink color is permanent.
3. Add 500 λ cerium carrier (10 drops) and 250 λ each (5 drops) of zirconium and lanthanum carriers, 7 ml of concentrated HNO₃, and 1 or 2 drops of H₂SO₃.*

*H₂SO₃ is preferable to H₂O₂ for reduction of cerium since H₂O₂ prevents carrying of niobium on Zr(IO₃)₄ precipitate.

4. Mix well and bring to a boil.
5. Add 20 ml of 0.35 M HIO_3 and cool in a water bath.
6. Centrifuge and transfer the supernatant liquid to another tube. Filter the $\text{Zr}(\text{IO}_3)_4$ precipitate, wash with iodate wash solution, alcohol, and ether, mount, and count for UX or Zr+Nb.
7. Add 1 scoop of KBrO_3 to the supernatant solution containing cerium. Stir and allow to stand for 2 min without heating.*
8. Filter through 2 disks of filter paper. Rinse the tube twice with the KIO_3 wash solution and filter rinses. Dry the precipitate by washing with methanol and ether. Mount precipitate.
9. After 2 hr, count through 353-mg/cm² aluminum absorber.
10. Calculate:

$$\text{ct/min/ml Ce-144} = \frac{\text{ct/min through 353-mg/cm}^2 \text{ Al} \times 2.9^{**}}{\text{ml sample}}$$

Cs-137 by Tetraphenylboron Precipitation

Principle of Method

Cesium reacts with sodium tetraphenylboron in dilute acid solutions to form a precipitate. Only a few other ions, such as potassium and ammonium, form precipitates with tetraphenylboron. Large amounts of lithium, sodium alkali earths, aluminum, chromium, zinc, or phosphorous do not interfere. (19, 20) The cesium yield depends on the acidity of the solution from which the precipitation takes place. The yield is 88% at 1.0 M HNO_3 , 96% at 0.5 M, and 99% at 0.2 M HNO_3 . With the method as written, the precipitate carries less than 1% of the radioactive zirconium, niobium, and rare earths present. The decontamination from ruthenium depends upon the state of the ruthenium in the sample. About 1% of the ruthenium was carried from tracer ruthenium and Thorex 1AF solutions, but about 5% was carried from a Coating Removal Solution (highly alkaline). If better decontamination from zirconium or niobium is required, a ferric hydroxide scavenge may be used.

Reagents

1. Mixed carrier solution, 10 mg Zr/ml, 5 mg La/ml, 5 mg Ru/ml, 10 mg Cs/ml, 6 M HNO_3 . Dissolve 2.94 g $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 1.55 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 1.0 g RuCl_3 , and 1.47 g CsNO_3 in 40 ml concentrated nitric acid and add this solution to 53 ml distilled water.

*Heating at this point is unnecessary and leads to precipitation of uranium. This is possible by the oxidation of IO_3^- to IO_4^- by BrO_3^- at elevated temperatures which results in precipitation of uranyl periodate.

**If the beta count through 1170 mg/cm² aluminum x 1.04 is subtracted from the 353 mg/cm² aluminum count before multiplying by 2.9, some additional counting df from gamma activities can be obtained. This has been found unnecessary in all cases except the determination of traces of cerium in pure Zr-Nb activity where a df of greater than 10³ is important.

2. Sodium tetraphenylboron, 0.1 M. Dissolve 3.4 g sodium tetraphenylboron in distilled water, add one drop 6 M NaOH, and dilute to 100 ml with distilled water.

Procedure

1. Place 1 ml mixed carrier solution and the sample in a dry 40-ml centrifuge tube (to prevent dilution).
2. Heat to boiling over a burner to promote exchange with carrier. Allow to stand 5 min.
3. Add 20 ml distilled water. Mix.
4. Add 1 ml 0.1 M sodium tetraphenylboron, mix well, and allow to stand 5 min.
5. Centrifuge, decant the solvent, and wash with water.
6. Centrifuge and decant water.
7. Slurry mount with water.
8. Use the spectrometer equation to determine the ct/min of cesium.*

$$\text{ct/min/ml Cs} = \frac{\text{ct/min Cs } \gamma}{\text{ml sample}}$$

Pa-233 by TTA Extraction

Principle of Method

When present in trace amounts, Pa-233 can be chemically separated from most other gamma activities before it is counted on the scintillation spectrometer. A separation is helpful since the photopeak occurs at 0.31 Mev, which is in the region of Compton scattering for most fission products or near the foot of the peak for Ce-144. (See Figure 7.)

The separation is accomplished by extraction from 6 M HNO₃ into 0.5 M TTA in 1 - hexanol.⁽⁵⁾ Decontamination factors for ruthenium, cerium, and cesium were greater than 100. Zr-Nb 95 must be corrected for. Protactinium must be separated before measurement on long-cooled slugs where it is a minor activity; only with short-cooled slugs where Pa is the principal activity can separation be avoided before measurement.

Apparatus and Reagents

1. Extraction vessel with stirrer
2. Heating block
3. Stainless steel dishes, 1-1/2 in.
4. 0.5 M TTA dissolved in 1 - hexanol (111 g/liter)

*An equation can be derived to correct the count at the Cs-137 peak for contributions due to Ru-103 and Zr-Nb-95. The equation will have the form:

$$\text{ct/min Cs} = A (\text{ct/min at 660 kev}) - B (\text{ct/min at 500 kev}) - C (\text{ct/min at 760 kev})$$

where A, B, and C are constants.

The constants can be determined by counting a Cs-137, Ru-103, and Zr-Nb-95 standard at each of the three peaks and solving the three equations in three unknowns. The value of the constants will depend upon the characteristics of the individual γ -ray spectrometer.

5. 6 M HNO_3 Procedure

1. Rinse the extraction vessel by filling to the side arm with acetone. Discard the acetone and fill the vessel with water. Repeat with a final acetone rinse.
2. Add 1.0 ml 6 M HNO_3 to extractor.
3. Discharge sample into above solution and flush the pipet two or three times to ensure complete sample transfer.
4. Stir the solution with the motor-driven stirrer for a few seconds to ensure complete mixing.
5. Add 1.0 ml 0.5 M TTA in 1 - hexanol and stir for 15 min at a rate to intermix the two phases thoroughly.
6. Allow the phases to separate cleanly and then carefully mount 500 λ of the organic phase on a 1-1/2-in. dish placed on the heating block.
7. Count for gamma at the protactinium and Zr-Nb photopeaks:*

$$\text{ct/min/ml Pa} = \text{Pa Factor} \frac{315 - \text{Fraction at } 315 \times 750}{\text{ml sample}}$$

Ru-106 by Direct ReductionPrinciple of Method

Ruthenium is reduced to the metallic state in HCl solution by the addition of elemental magnesium. Since the reduced ruthenium may be contaminated with colloidal niobium and zirconium if they are present in the sample, the beta count is made through a 353-mg/cm² aluminum absorber which absorbs weak betas from ruthenium and contaminants. This count then consists of the attenuated betas of the Rh-106 daughter. Multiplication by the proper absorber factor (2.2) converts the attenuated Rh-106 count to an equivalent Ru-106 count.

A gamma count as well can be taken on the gamma scintillation spectrometer. A count is made at the ruthenium photopeak (around 500 kev) which includes the 500 kev gamma energies from Ru-103 and Ru-106. A count at the Zr-Nb photopeak is then made to obtain the Zr-Nb Compton correction to be applied under the ruthenium photopeak (see page 21). Multiplication by the ruthenium factor then gives the Ru-106 + Ru-103 gamma count corrected to 10% gross gamma counting efficiency.

Nitrate ion interferes if present in large amounts, since it is reduced to nitrite ion by action of magnesium and subsequently complexes ruthenium. A maximum of 50 μ moles of thorium nitrate (25 λ of 2 M) can be tolerated.

*A more detailed description of this technique will be found under Radiation Measurements, Gamma Scintillation Spectrometry.

This method is used for both aqueous and TBP phases. Typical decontamination factors are as follows:

<u>Isotope</u>	<u>Chemical df</u>	<u>Counting df (β)</u>	<u>Total df</u>
Zr-Nb	20-40	60	1200-2400
Ce	2000	1.5	3000
Cs	2000	50	100,000
Sr	2000	13	26,000
UX	30	2.8	84
Pa	60	1000	60,000

Reagents and Apparatus

1. Concentrated and 6 M HCl
2. Magnesium metal turnings, cp
3. 10% $\text{H}_2\text{C}_2\text{O}_4$
4. Diethyl ether
5. Methanol
6. Zirconyl chloride carrier. Dissolve 35 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 80 ml of concentrated HCl. Make up to 1 liter with water.
7. Ce^{+4} sulfate carrier. Dissolve 25 g of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in 30 ml of concentrated H_2SO_4 . Add 20 ml of H_2O slowly with stirring. Cool the mixture to room temperature and filter. Dilute the filtered solution to 1 liter with water.
8. Ruthenium chloride carrier. Dissolve 25 g of $\text{RuCl}_4 \cdot x\text{H}_2\text{O}$ in 250 ml of water containing 25 ml concentrated HCl. Dilute to 1 liter with water.
9. 2 M $\text{Fe}(\text{SO}_3\text{NH}_2)_2$ (ferrous sulfamate)
10. 24-mm filter paper (S and S No. 507 or Whatman No. 50)

Procedure

1. Add the sample to 1 ml of concentrated HCl in a 50-ml centrifuge tube.
2. Add 500 λ of ruthenium carrier and 1 drop each of $\text{Ce}(\text{IV})$ and ZrO^{+2} holdback carriers. Warm for some time to promote exchange with the carriers.
3. Add 100 λ of 2 M $\text{Fe}(\text{SO}_3\text{NH}_2)_2$ (Optional. Added to reduce interference from nitrite complexing.)
4. Dilute to 10 ml with distilled water.
5. Slowly add magnesium metal turnings, until the metal is in excess and the ruthenium carrier is completely reduced to metal.
6. Add increments of 6 M HCl at the rate of 10 drops at a time until the excess magnesium is dissolved.
7. Filter the solution through 2 disks of filter paper.
8. Rinse the tube with 6 M HCl. Filter the rinses.
9. Wash the precipitate on the paper with 5 ml of 10% H_2SO_4 to remove traces of cerium.

10. Wash the precipitate with 5 ml of 10% $\text{H}_2\text{C}_2\text{O}_4$ to remove traces of zirconium and niobium.
11. Dry the paper with methanol and ether. Mount and count for betas through a 353-mg/cm² aluminum absorber or for gammas on the gamma scintillation spectrometer.
12. Calculate:

$$\text{ct/min/ml Ru-106} = \frac{\beta \text{ ct/min thru } 353 \text{ mg/cm}^2 \text{ Al} \times 2.2^*}{\text{ml sample}}$$

$$\text{ct/min/ml Ru-103} + \text{Ru-106} = \frac{\text{Ru factor } (500 - \text{Fraction at } 500 \times 760)^{**}}{\text{ml sample}}$$

Ru-106 by Distillation

Principle of Method

Ruthenium is separated cleanly from other fission products by distillation as RuO_4 from HClO_4 .⁽²¹⁾ To prevent volatilization of iodine, carrier is added and sodium bismuthate included to oxidize iodine to nonvolatile IO_3^- or IO_4^- . The presence of phosphate prevents the volatilization of small amounts of molybdenum. The RuO_4 is caught in NaOH solution, and ruthenium is precipitated in the basic solution as a mixture of Ru_2O_3 and RuO_2 by reduction with ethanol. The ruthenium oxide precipitate is dissolved in HCl , reduced with magnesium metal, and mounted for counting.

This procedure is used for the preparation of a ruthenium standard plate from which the gamma scintillation spectrometer is calibrated. Slugs with differing pile histories and cooling periods before solvent extraction have differing Ru-103 to Ru-106 ratios, hence differing gamma-to-beta ratios. A ruthenium plate clean of other activities must be used for each new dissolving, therefore, to obtain counting factors for ruthenium samples run on that dissolving.

Apparatus and Reagents

1. Distillation flask, the pot of about 50-cc capacity, containing a glass delivery tube which will be immersed in a 50-ml centrifuge tube containing caustic. An arrangement for bubbling air (1 to 2 bubbles per sec) is necessary to prevent bumping while the distillation is in progress.

*If the beta count through 1170-mg/cm² aluminum x 1.04 is subtracted from the 353-mg/cm² aluminum count before multiplying by 2.2, some additional counting df from gamma activities can be obtained. This has been unnecessary in all cases except in the determination of traces of ruthenium in pure Zr-Nb activity where a df greater than 10^3 is important.

**A more detailed description of this technique will be found under Radiation Measurements, Gamma Scintillation Spectrometry.

2. 6 M NaOH
3. 6 M HCl
4. 70% HClO_4
5. 85% H_3PO_4
6. NaBiO_3
7. 0.1 M KI
8. Magnesium metal
9. Ruthenium carrier, 10 mg Ru/ml
10. Ethanol

Procedure

1. Place about 12 ml of 6 M NaOH in a 50-ml centrifuge tube and put it under the delivery tube of the distillation flask.
2. Add to the distillation flask:
 - 2 ml ruthenium carrier
 - Sample
 - 1 ml 0.1 M KI
 - 0.5 g NaBiO_3
 - 1 ml conc H_3PO_4
 - 10 ml conc HClO_4
3. Let stand 10 min to ensure complete oxidation of iodine. Then allow air to pass through the flask. Heat gently to boiling, then boil vigorously until white fumes of HClO_4 come over. Continue distilling 1 to 2 ml HClO_4 . The solution in the flask should be colorless.
4. Remove the centrifuge tube containing distilled ruthenium, add about 3 ml ethanol, heat just to boiling, and centrifuge. The supernate should be colorless. If not, reneutralize with concentrated HCl, add 1 ml 6 M NaOH, and reheat with alcohol.
5. Discard supernate. Add 2 ml 6 M HCl and 10 ml water. Reduce with magnesium metal under the conditions given on page 30. (Reduction Method)

Sr-89 by Fuming Nitric Acid Precipitation

Principle of Method

Strontium is separated from other activities by the precipitation of the nitrate from fuming nitric acid solution. The precipitate is then dissolved, and the solution scavenged by a ferric hydroxide precipitation. Strontium is then reprecipitated as the oxalate for mounting and counting. A typical decontamination factor from all other fission products is greater than 2000.

If barium is known to be present, the procedure for separating strontium from barium given in CN-2815(21) should be used.

Reagents and Apparatus

1. Strontium carrier, 10 mg Sr/ml
2. Fuming HNO_3
3. Fe^{+3} carrier, 10 mg Fe/ml
4. 6 M NH_4OH
5. Methyl red indicator
6. 6 M HNO_3
7. NH_4OH , conc
8. Saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution
9. 24-mm filter paper disks (S and S No. 507 or Whatman No. 50)

Procedure

1. In a 50-ml centrifuge cone place 3 ml of strontium carrier, the sample, and 25 ml of fuming HNO_3 .
2. Cool for 2 min, centrifuge, and discard the supernatant liquid.
3. Dissolve the precipitate in 2 ml of H_2O (heat if necessary) and reprecipitate the strontium with 15 ml of fuming HNO_3 .
4. Centrifuge and discard the supernatant liquid.
5. Dissolve the precipitate in 5 to 10 ml of H_2O and add 10 drops of Fe^{+3} carrier. While stirring add 6 M NH_4OH in drops until $\text{Fe}(\text{OH})_3$ precipitates, and add 10 drops excess.
6. Centrifuge and decant the supernatant liquid to a new tube. Discard the precipitate.
7. Add a drop of methyl red indicator to the solution and add 6 M HNO_3 until its color changes to red.
8. Add 2 ml of concentrated NH_4OH . Heat nearly to boiling and add 5 ml of saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in drops while stirring the solution. Stir, then cool for 10 min.
9. Filter the strontium oxalate through 2 disks of filter paper.
10. Wash the precipitate with water, methanol, and ether.
11. Mount and count for beta.

$$\text{ct/min/ml Sr-89} = \frac{\text{ct/min}}{\text{ml sample}}$$

Th-234 (UX_1) by Iodate Precipitation

Principle of Method

Thorium, protactinium, zirconium, and niobium are precipitated on zirconium iodate in the procedure for the determination of Ce-144 (see page 27). This precipitate is mounted and counted for betas through 57-mg/cm² aluminum which absorbs the beta from Zr-95 + Nb-95, Th-234, and Pa-233. The

count then consists of the attenuated betas of the Pa-234 daughter of Th-234. This beta count is multiplied by the appropriate absorber factor (1.4) in order to obtain the corrected Pa-234 count which is equivalent to the Th-234 activity. Typical total decontamination factors are 30 to 100 from Ce-144, Ru-106, Pa-233, and Zr-95 + Nb-95.

Reagents and Apparatus

1. KIO₃ wash: 8 g of KIO₃ and 50 ml of concentrated HNO₃, diluted to 1 liter.
2. 24-mm filter paper (S and S No. 507 or Whatman No. 50).

Procedure

1. To the zirconium iodate precipitate obtained in Step 6 of the Ce-144 procedure (see page 27), add approximately 5 ml of KIO₃ wash. Stir up the precipitate and filter through 2 disks of filter paper. Rinse the centrifuge tube with KIO₃ wash and add the rinsings to the filter.
2. Wash the precipitate with methanol and ether, and dry by suction.
3. Mount and count for beta through 57-mg/cm² aluminum absorber.*

$$\text{ct/min/ml Th-234} = \frac{\text{ct/min through 57-mg/cm}^2 \text{ Al} \times 1.4}{\text{ml sample}}$$

Th-234 by Mesityl Oxide Extraction

Principle of Method

The substitution of an extraction method⁽¹⁶⁾ for Th-234 for the precipitation method is attractive by virtue of its quickness and ease. A ruthenium holdback carrier and a small amount of phosphate is added to reduce the extraction coefficient of ruthenium and other fission-product activities. Extraction into mesityl oxide is made from an aqueous phase highly salted with LiNO₃. An aliquot of the organic phase is mounted for direct beta counting. Decontamination factors from all fission products are on the order of 80 to 100. This procedure is used only in LBT streams.

Apparatus and Reagents

1. Extraction vessel with stirrer
2. 4.0 M LiNO₃
3. Mesityl oxide

*If the beta count through 1170-mg/cm² aluminum x 1.04 is subtracted from the 57-mg/cm² aluminum count before multiplying by 1.4, some additional counting df from gamma activities can be obtained. This has been found unnecessary in all cases except the determination of traces of impurities in the presence of much Zr + Nb activity where a df of greater than 100 is important.

4. Ruthenium carrier, 10 mg Ru/ml
5. 0.1 M KH_2PO_4
6. HNO_3 , conc
7. Heating block
8. Stainless steel dishes, 1-1/2 in.

Procedure

1. Rinse the extraction vessel by filling to the side arm with acetone. Discard the acetone and fill the vessel with water. Repeat with a final acetone rinse.
2. Add 2.0 ml of 4.0 M LiNO_3 , 25 μ KH_2PO_4 , and 50 μ conc HNO_3 to extractor.
3. Discharge LBT sample into the above solution and flush the pipet two or three times to ensure complete sample transfer.
4. Stir the solution with the motor-driven stirrer for a few seconds to ensure complete mixing.
5. Add 2.0 ml mesityl oxide and stir for 2 min at a rate to intermix the two phases thoroughly.
6. Allow the phases to separate cleanly and then carefully mount 500 μ of the mesityl oxide phase on a 1-1/2-in. dish on the heating block.
7. Count for betas through a 57-mg/cm² aluminum absorber

$$\text{ct/min/ml Th-234} = \frac{\text{count through 57-mg/cm}^2 \text{ Al} \times 1.4}{\text{ml sample}}$$

Total Rare Earths by Iodate-Oxalate Method

Principle of Method

Rare earths in samples are made free of zirconium, niobium, and UX by zirconium iodate. Scavenging of UX_1 , a major contributor to activity, is repeated to effect a good separation. Hydroxide precipitation separates rare earths from alkaline earths. Finally, the rare earths are converted to the oxalate and counted for beta activity. Decontamination factors are on the order of 200 for ruthenium, 600 for strontium, and greater than 1000 for UX_1 , Zr-Nb, and protactinium.

Apparatus and Reagents

1. Clinical centrifuge
2. 50-ml centrifuge tubes
3. Sand bath
4. 24-mm filter paper (S and S No. 507 or Whatman No. 50)
5. Cerium carrier, 10 mg/ml
6. Zirconium carrier, 10 mg/ml
7. HNO_3 , conc
8. Conc and 6 M HCl

9. 0.35 M HIO_3
10. Metacresol purple indicator
11. 12 M NaOH
12. 6% H_2SO_3
13. NH_4OH , conc
14. Ethanol
15. Ether

Procedure

1. Place 2.0 ml of cerium carrier and the sample in a 50-ml centrifuge tube.
2. Add 2 drops zirconium carrier, and 5 drops H_2SO_3 , and mix well.
3. Add 5.0 ml concentrated HNO_3 , mix, and bring to a boil in a sand bath continuously to prevent bumping.
4. Add 20 ml 0.35 M HIO_3 and cool.
5. Centrifuge and transfer only the supernatant solution to another tube. Be careful to transfer no precipitate since it contains the UX_1 activity.
6. Add 8 to 10 drops zirconium carrier slowly with intermittent stirring. Centrifuge and transfer supernate to another tube. Again be careful to transfer no precipitate.
7. Add 6 drops of metacresol purple and cautiously neutralize and precipitate the solution with 12 M NaOH (Considerable heat evolved may affect the indicator, so more indicator may be needed near the end point.)
8. Centrifuge and discard supernate.
9. Dissolve the precipitate in 3.0 ml concentrated HCl, dilute to about 8 ml, and add H_2SO_3 in drops until any dark brown iodine color which may develop is decolorized. Add 5 drops excess H_2SO_3 .
10. Dilute to about 15 ml and then precipitate with about 5 ml concentrated NH_4OH . Centrifuge and discard supernate.
11. Dissolve the precipitate in 1 ml 6 M HCl. Add 15 ml distilled water, heat to boiling, and add 15 ml 10% oxalic acid. Cool in water for 10 min.
12. Filter through 24-mm filter paper. Rinse with water, ethanol, and ether.
13. Count directly for beta:

$$\text{TRE } \beta = \frac{\beta \text{ ct/min}}{\text{ml sample}}$$

Total Rare Earths and UX by Oxalate Precipitation

Principle of Method

In streams where UX activities are negligible compared with activities of the rare earths, it is possible to omit most of the separation steps usually employed. A single oxalate precipitation is a rapid method for rare earths. Typical decontamination factors are:

<u>Isotope</u>	<u>Chemical df</u>	<u>Counting df</u>	<u>Total df</u>
Zr-Nb	200	20	4000
Sr	3	1	3
Cs	800	3	2400
Ru	1400	1	1400
Pa	200	20	4000

Reagents and Apparatus

1. 10% oxalic acid
2. 6 M HCl
3. Ce⁴⁺ carrier, 10 mg/ml
4. 24-mm filter paper (S and S No. 507 or Whatman No. 50)

Procedure

1. To a 50-ml centrifuge cone add 1 ml of 6 M HCl, 2 ml of cerium carrier, and 15 ml of water.
2. Add the sample and heat to boiling.
3. Add 15 ml of 10% H₂C₂O₄, mix, and cool for 10 min in a water bath.
4. Filter through two disks of very retentive filter paper.
5. Wash with water, methanol, and ether.
6. Mount and count for beta without an added aluminum absorber.

$$\text{ct/min/ml (TRE + UX } \beta) = \frac{\beta \text{ ct/min}}{\text{ml sample}}$$

Zr-95 + Nb-95 by Iodate Precipitation

Principle of Method

Zirconium and niobium are most easily determined as the insoluble iodates. This precipitate is filtered, mounted, and counted for gamma on the scintillation spectrometer. Typical decontamination factors are 100 to 500 for rare earths and strontium, and greater than 2000 for cesium and ruthenium.

The presence of fluoride or other "complexers" causes incomplete precipitation of the iodate; when it is known to be present, the Zr-Nb must first be separated by caustic precipitation.

Reagents and Apparatus

1. KIO_3 wash solution. 8 g KIO_3 , 50 ml conc HNO_3 , diluted to 1 liter.
2. 24-mm filter paper (S and S No. 507 or Whatman No. 50)

Procedure

1. To the zirconium iodate precipitate obtained in Step 6 of the procedure for Ce-144 (see page 27), add about 5 ml of KIO_3 wash. Stir the precipitate and filter through two disks of filter paper. Rinse the centrifuge tube with KIO_3 wash and add the rinsings to the filter.
2. Wash the precipitate with methanol and ether, and dry by suction.
3. Count for gamma on the scintillation spectrometer:

$$\text{Zr-Nb} = \frac{\text{Zr-Nb factor (count at Zr-Nb photopeak)*}}{\text{ml sample}}$$

Special Fission-Product Determination from a Gross Mount by Gamma Scintillation Spectrometry

It is possible to carry out many of the radiochemical analyses of gamma emitters in Thorex streams on the spectrometer without first performing any chemical separation. (5,12,13,22)

All the calculations described will give the corrected count for the activity under consideration at its principal photopeak. This corrected count is adjusted to 10% Cs-137 counting yield with a factor obtained by dividing the count of the pure activity at its photopeak into the gross gamma count at 10% Cs-137 counting efficiency.

Spectra for most of the pure activities encountered in Thorex streams can be normalized to unity at their principal photopeak. Certain photopeaks, such as those of Zr-95 + Nb-95 and Cs-137, are not completely resolved. Furthermore, Compton scattering from more energetic gamma emitters must be compensated for.

Compensation for Compton scattering and incomplete resolution is most conveniently accomplished by solution of simultaneous equations. As an example, let us consider a short-cooled slug whose major gamma activities on a direct mount are Zr-95 + Nb-95, Ru-103, and Pa-233. The following table

*A more detailed description of this counting technique will be found under Radiation Measurements, Gamma Scintillation Spectrometry.

lists the amount of each activity normalized to unity at the principal photopeak that appears under the other photopeaks.

Fraction of Activity at Various Photopeaks

<u>Photopeak, kev</u>	<u>Zr-95 + Nb-95</u>	<u>Ru-103</u>	<u>Pa-233</u>
760	1.000	0.009	0.005
490	0.421	1.000	0.003
315	0.643	0.348	1.000

Then, the total counting rate at each photopeak can be stated of follows:

$$\begin{aligned} \text{Total counting rate at 760 kev} &= 1.000 \text{ Zr-Nb} + 0.009 \text{ Ru} + 0.005 \text{ Pa} & (1) \\ \text{Total counting rate at 490 kev} &= 0.421 \text{ Zr-Nb} + 1.000 \text{ Ru} + 0.003 \text{ Pa} & (2) \\ \text{Total counting rate at 315 kev} &= 0.643 \text{ Zr-Nb} + 0.348 \text{ Ru} + 1.000 \text{ Pa} & (3) \end{aligned}$$

Solving these equations simultaneously, we obtain:

$$\begin{aligned} \text{Zr-Nb} &= 1.006 \overline{(760)} - 0.007 \overline{(490)} - 0.005 \overline{(315)} & (4) \\ \text{Ru} &= 1.004 \overline{(490)} - 0.423 \overline{(760)} - 0.001 \overline{(315)} & (5) \\ \text{Pa} &= 1.003 \overline{(315)} - 0.499 \overline{(760)} - 0.344 \overline{(490)} & (6) \end{aligned}$$

where $\overline{760}$, $\overline{490}$, and $\overline{315}$ represent the expressions to the left of the equals sign in Equations 1, 2, and 3.

These considerations do not apply for the determination of Pa-233 in long-cooled slugs since Ce-144 becomes the major gamma activity, and incomplete resolution and tailing at the photopeak interferes with protactinium at its photopeak. In these cases, the extraction technique must be used to decontaminate from cerium. (See Figure 7.)

MISCELLANEOUS DETERMINATIONS

n-Butanol (Colorimetric)

Principle of Method

One of the hydrolysis products formed on decomposition of TBP is n-butanol which is only slightly soluble in water and is not efficiently removed by solvent wash. A 30% TBP solution with 0.5% butanol added still contained 0.48% butanol after the caustic wash cycle. A dichromate colorimetric method^(23,24) similar to that used for methyl isobutyl carbinol in hexone is used to determine n-butanol; the method is more easily handled for TBP than for hexone since TBP is more resistant to oxidation. The reaction goes to completion with the alcohol undergoing a 4-electron change.

Some dichromate extracts into the organic phase, but all the Cr^{+3} formed is found in the aqueous layer where it is measured. The reaction is complete in 5 min of mixing and does not proceed further even after 1 hr of additional mixing. The blank is very low for vacuum-distilled TBP ($< 0.004\%$ butanol).

Reagents and Apparatus

1. Dichromate reagent, $0.02 \text{ M K}_2\text{Cr}_2\text{O}_7$ in 4 M HNO_3 (for use up to $0.2 \text{ vol } \% \text{ n-butanol}$)
2. Centrifuge
3. Beckman spectrophotometer

Procedure

1. Place a 5-ml TBP sample and a 5-ml dichromate reagent in a 15-ml cone.
2. Equilibrate the phases thoroughly with a spiral glass stirrer for at least 5 min.
3. Centrifuge the phases apart.
4. Pipet the bottom phase directly into a 1-cm cell and read the optical density at $580 \text{ m}\mu$ against water.

$$\text{Vol } \% \text{ of butanol} = 0.50 (\text{O.D. at } 580 \text{ m}\mu).*$$

Dibutyl Phosphate (Trace Analysis)

Principle of Method

DBP forms a very stable uranium complex which is extractable into the organic phase from dilute uranium solutions. The complex contains 1 mole of uranium to 2 moles of DBP. An organic sample ($30\% \text{ TBP-Amsco}$) is contacted with an equal volume of 0.002 M neutral UNH, and the uranium molarity of the organic phase is measured fluorimetrically.⁽²⁵⁾

$$\frac{\text{mg DBP}}{\text{kg sol}} = \frac{\text{moles U}}{\text{liter sol}} \times \frac{2 \text{ moles DBP}}{1 \text{ mole U}} \times \frac{211 \text{ g DBP}}{1 \text{ mole DBP}} \times \frac{1000 \text{ mg DBP}}{1 \text{ g DBP}} \times \frac{1 \text{ liter sol}}{0.840 \text{ kg sol}}$$

$$\text{ppm DBP} = (5 \times 10^5) (\text{U molarity})$$

Known solutions have been run by this method with the following results:

<u>DBP Added, ppm</u>	<u>Uranium, Molarity</u>	<u>DBP Found, ppm</u>
0	5.94×10^{-6}	3
10	2.33×10^{-5}	12
50	1.04×10^{-4}	52
100	2.12×10^{-4}	106
250	5.05×10^{-4}	252
500	1.05×10^{-3}	530

*If optical density exceeds 0.4, all the dichromate has been consumed and a stronger dichromate reagent must be prepared. To date no sample has been found with sufficient butanol to require this.

The applicable range can be lowered or raised by corresponding lowering or raising of uranium molarity in the aqueous phase. Hence, for 0.1 to 5 ppm DBP, equilibrate with 0.00002 M neutral UNH. The method is applicable to neutral LAX organic (30% DBP-Amsco) samples.

Apparatus and Reagents

1. Test tubes, 12 x 75 mm, 3 ml
2. UNH solutions in water, 0.002 M and 0.00002 M
3. Micropipets, 1000 and 50 λ
4. Mechanical stirrer
5. Centrifuge
6. Fluorimeter

Procedure

1. Place 1000 λ of the 0.002 M uranium solution in a 3-ml centrifuge cone.
2. Add 1000 λ of the organic sample.
3. Equilibrate the solutions by stirring the well intermixed phases for 5 min.
4. Centrifuge for 2 to 3 min to separate the two phases. Discard aqueous.
5. Scrub organic phase twice with 1000 λ of 0.00002 M UNH.
6. Make three 50 λ direct mounts of the organic layer for uranium determination (see page 23). If the sample contains more than 100 ppm DBP it will be necessary to make a dilution of the organic phase. Dilute 500 λ to 5.0 ml with hexone and make three 50 λ mounts as before. If the sample contains over 500 ppm of DBP it is necessary to dilute original samples 10X with Amsco before analysis.

$$\text{ppm DBP} = (5 \times 10^5) (\text{M uranium found})$$

Fluoride Ion

Principle of Method

Fluoride ion in a Thorex sample is complexed with the thorium and aluminum present in the solution. A large added excess of phosphoric acid reacts with the thorium and aluminum to free the fluoride, which then reacts with the glass container to form silicon tetrafluoride.^(1,13) Silicon tetrafluoride distills from perchloric acid solutions at temperatures above 125°C. In the condensate, the silicon tetrafluoride reacts with water to form H_2SiF_6 and hydrous silica. The H_2SiF_6 is appreciably ionized, and when a mixture of thorium and Thoron is added, the fluoride complexes some of the thorium. The loss in color of the thorium-Thoron lake is a measure of the amount of fluoride present. The intensity of the lake is also dependent on the final acidity of the solution, therefore, the condensate is neutralized before the addition of the thorium and Thoron reagent solutions. The final acidity must be 0.05 - 0.10 M from the HCl in the reagents.

Reagent Solutions

- Thoron solution (0.01% Thoron) - 0.050 g Thoron diluted to 500 ml with distilled water (see page 13)
- Thorium solution (8.8×10^{-4} M Th) - 100 λ of 2.2 M Th stock diluted to 250 ml with 1 M HCl.
- Fluoride standard solution (0.01 M NaF) - 0.210 g NaF diluted to 500 ml with distilled water and stored in a plastic bottle.

Apparatus

1. Distillation flask, 50 ml
2. Volumetric flask, 50 ml
3. Water-cooled condenser, 50 ml
4. Beckman spectrophotometer

Procedure

1. Rinse the apparatus thoroughly with water. Place 50 ml volumetric flask with a funnel at end of condenser.
2. Place in distillation flask 3 or 4 capillary tubes (2 in. long with one end sealed and open end downward) to prevent bumping, plus the following:
 - Several glass beads
 - 10 ml water
 - 5 ml conc perchloric acid
 - 100 λ conc phosphoric acid
 - sample (0.2 to 2.0 μ moles fluoride)
3. Distill until thermometer reading reaches 150°C. The temperature will remain at 100°C until most of the water has distilled off and then rise rapidly to 200°C.
4. Disconnect distillation flask from condenser and rinse condenser with distilled water, allowing the water to drain into the volumetric flask.
5. To the volumetric add:
 - One drop phenolphthalien
 - 500 λ 6 M NaOH
 - Mix (if solution is not basic, add more 6 M NaOH in drops to the red end point)
6. Carefully neutralize to colorless end point with 1 M HClO₄.
7. Add 3 ml thorium solution.
8. Add 3 ml Thoron solution.

9. Dilute to the mark with distilled water and mix.
10. Read optical density on the Beckman spectrophotometer at 550 mμ against water with 10.0-cm cells.
11. Read μ moles fluoride from curve.*
12. Calculate:

$$\underline{\text{M Fluoride}} = \frac{\mu\text{moles F} \times \text{dil factor}}{\lambda \text{ sample}}$$

Uranium (Fluorimetric Method)

Principle of Method

Fusions of sodium fluoride containing small amounts of uranium show a green fluorescence under ultraviolet illumination. The intensity of fluorescence is directly proportional to the amount of uranium present from 0 to 5 μg U/80 mg NaF. The blank due to reagent is about 0.0007 μg U per 80 mg NaF. Analyses are run in triplicate or quadruplicate. The method⁽²⁶⁾ is applicable to aqueous or organic samples if U-238 is used instead of U-233. Where U-233 is the principal uranium isotope counting techniques are preferable.

In the fluorimetric determination of uranium, many metals including thorium interfere by quenching the fluorescence. The extent of interference due to thorium has been measured. The number of micrograms of thorium per fusion of 80 mg NaF and the corresponding per cent quenching is given in Table 1.

TABLE 1. Quenching of Uranium Fluorescence by Thorium

<u>μg Th/Fusion</u>	<u>% Quenching</u>
6090	88
3050	85
1520	82
760	75
380	68
190	60
95	48
48	34
21	25
15	10

*Curve is obtained by running a zero fluoride (steps 7 to 10), 100λ 0.01 M NaF standard (steps 7 to 10), and reagent blank (steps 8 to 10). Subtract the reagent blank (~ 0.080 O.D. units) from all readings. Plot on semi-log paper the optical density of the zero fluoride and one μmole fluoride against the μmoles fluoride on the linear scale. Connect the two points with a straight line.

This quenching effect can be reduced by dilution of the sample or separation of the thorium and uranium. Hexone extraction of uranium from aluminum nitrate has been used for this purpose. The distribution ratios of uranium and thorium between hexone and aluminum nitrate were measured under two sets of conditions.

TABLE 2. Extraction Coefficient of Uranium and Thorium

<u>Conditions</u>	<u>E (org/aq) Uranium</u>	<u>E (org/aq) Uranium</u>
1.9 M Al (NO ₃) ₃ } -0.2 M HNO ₃	7.5	0.22
1.6 M Al (NO ₃) ₃ } 0.0 M HNO ₃	7.5	0.20

Each value given in Table 2 is the average of three to five measurements. The separation is not a clean-cut one and it is necessary to perform an extraction followed by as many as three fresh equal volume aqueous scrubs to effect 99.84% - 99.92% removal of thorium and a 60% recovery of uranium.

Apparatus and Reagents

1. Fluorimeter
2. Platinum fluorimeter dishes
3. Standard uranium glass
4. Meeker burner and fusion device
5. Infrared lamp
6. Sodium fluoride selected for high purity and low uranium content, and a glass scoop to deliver 80+10 mg of NaF.
7. Dilute HNO₃ wash solution (0.1 N)
8. Separation reagent, 49 ml of 1.6 M Al(NO₃)₃ (neutral) d=1.250, ph = 0.75
1 ml of 1 M AgNO₃. Contact each batch with fresh hexone to remove uranium contamination. Discard the hexone phase.

Procedure

A. In the Absence of Chromium, Iron, Thorium, and Radioactivity

1. Clean the platinum dishes by boiling for 1 hr in citric acid solution.
2. Deliver suitable aliquots to the dishes.
3. Evaporate the sample to dryness under a heat lamp.
4. Add 80 + 10 mg of NaF from a special scoop.
5. Place the dish on a fusion device.
6. Fuse with a Meeker burner until the melt becomes clear.
The use of didymium goggles reduces sodium glare and makes observation easier.

7. Allow the melt to cool and then fuse a second time to make the melt uniform.
8. When the melt is cool, read in the fluorimeter promptly, since upon long standing the samples absorb water and increase slightly in fluorescence.
9. Calculations:

$$K = \frac{\mu\text{moles U in the standard}}{G \times S}$$

$$\underline{M} \text{ uranium} = \frac{G \times S \times K}{\lambda \text{ sample}}$$

where G is the galvanometer reading

S is the sensitivity factor (sensitivity setting/shunt setting)

K is the micromolar coefficient obtained from a standard uranium glass reading.

B. In the Presence of Chromium, Iron, Thorium, or Radioactivity

1. Flush a sample into 2 ml of the separation reagent in a 5-ml test tube.
2. Add 500 λ of hexone.
3. Mix with a motor-driven stirrer for at least 2 min making certain that both phases are so intermixed that no interface is observable.
4. Centrifuge 2 min to separate phases. Scrub with fresh reagent if necessary.
5. Pipet an aliquot of the hexone phase onto each of four fused blanks which had been read previously.
6. Read the plates on the fluorimeter and calculate:

$$\underline{M} \text{ uranium} = \frac{[(G \times S) \text{ Sample} - (G \times S) \text{ blank}] \times K}{\lambda \text{ sample}}$$

Manganese Dioxide (Direct Absorbance Measurement)

Principle of Method

Manganese dioxide concentration can be determined in "cold" thorium centrifuge effluent solutions directly by turbidimetric measurements with the Klett-Summerson colorimeter.⁽²⁵⁾ Concentrations within the range of 0.2 to 4.0 x 10⁻⁴ M can be accurately determined since the concentration of manganese dioxide is proportional to the turbidity of the solution. A straight line is produced by plotting the Klett reading of the solution vs the known concentrations.

Apparatus

Klett-Summerson photoelectric colorimeter with 690-m μ filter and 4-cm cell.

Reagents

None

Procedure

1. Insert a 690-m μ filter and turn on the colorimeter. Pull out the adapter compensator knob on the left of the Klett, fill the 4-cm cell with H₂O, and balance the instrument at 0.
2. Shake the solution thoroughly and pour 50 ml into the 4-cm cell.
3. Remove any bubbles from the solution.
4. Insert the cell in the instrument and take the Klett reading immediately.
5. Calculate the total number of micromoles of MnO₂ in the cell by dividing the Klett reading by 110. (1 μ mole MnO₂ reads 110).

$$M \text{ MnO}_2 = \frac{\mu\text{moles MnO}_2 \times 1000}{50 \text{ ml sample}}$$

Manganese Dioxide (Colorimetric)

Principle of Method

Manganese dioxide is removed from "cold" thorium centrifuge effluent solution by filtration with filter paper pulp on a fine sintered glass crucible. After thorough washing, the manganese dioxide is dissolved off the filter with 1 M HNO_3 acid containing hydrogen peroxide which reduces the manganese dioxide to manganous ions. After the filter is washed, the solution is boiled in the presence of platinum wire to decompose the excess hydrogen peroxide. Periodic acid is then added to oxidize the manganous ions to permanganate ions which are colored; the coloration can be read quantitatively with the Klett colorimeter. It is necessary to boil for 7 to 10 min to complete this oxidation. Failure to boil for this length of time may result in incomplete oxidation. It is known that the presence of citrate will reduce part of the permanganate and thus give low results amounting to an appreciable error. It is therefore imperative that all citrate be destroyed or removed before this oxidation is attempted.

Apparatus

1. Filtrator
2. Sintered glass crucible (fine) and holders
3. Filter paper pulp
4. Hot plate
5. Klett-Summerson photoelectric colorimeter
6. 540-m μ filter
7. 4-cm cell

Reagents

1. 1.0 M HNO_3 containing 5 drops of 30% H_2O_2 per 100 ml of solution
2. Crystalline HIO_4 (periodic acid)

Procedure

1. Set the filter paper pulp in the crucible with water, making a filter approximately 1/4 in. thick.
2. Pipet the sample onto the filter, making sure that filter mat remains intact. The following sample sizes will produce a color which will be within the accurate range of the colorimeter.

<u>Anticipated Concentration x 10⁻⁴ M</u>	<u>Sample Size, ml</u>
0.10 - 0.75	50
0.75 - 2.0	25
2.0 - 5.0	10
5.0 - 10.0	5
10.0 - 25.0	2

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3. Wash the filtrate three times with H_2O to remove all manganous ions, uranium, and citrate.
4. Place a clean 150-ml beaker in the filtrator and dissolve the manganese dioxide off the filter with 5 ml of the $HNO_3-H_2O_2$ solution.
5. Add water, then stir the filter pulp until all the precipitate is dissolved. Add more $HNO_3-H_2O_2$ if necessary.
6. After the solution has been filtered, wash the filter pulp thoroughly with water.
7. Add a coil of platinum wire to the solution and boil 2 min to decompose the excess H_2O_2 .
8. Remove the beaker from the hot plate (important) and add 1 scoop (0.3 to 0.4g) of HIO_4 .
9. Boil the solution for 7 to 10 min, cool, and dilute to 50 ml in a volumetric flask.
10. Place a 4-cm Klett cell containing 50 ml of H_2O in the colorimeter. Insert the 540-m μ filter in the holder. Balance the instrument to 0 using the water blank. Read the sample.
11. Obtain the number of μ moles of MnO_2 by dividing the Klett reading by 80 (1 μ mole MnO_2 reads 80)
12. Calculations

$$\underline{M MnO_2} = \frac{\text{mole Mn}}{\lambda \text{ of sample}}$$

Total Dissolved Manganese (Colorimetric)

Principle of Method

In the head-end process it is sometimes of interest to determine total dissolved manganese in order to obtain a manganese material balance since some MnO_2 cake is dissolved by radiation-induced H_2O_2 in water. Manganese is oxidized to permanganate by the action of ammonium persulfate with silver nitrate as catalyst^(27,28) and the color due to permanganate ion is measured in a filter colorimeter at 540m μ . Since most of the samples are highly radioactive, the method has been scaled down and transfers eliminated. Chlorides interfere with the method. Amounts of citrate, hydrogen peroxide, ferrous ion, or nitrite ion which might be used in cake dissolution samples have been shown not to interfere, at least in concentrations up to 1 M and for thorium up to 2.5 M in the original sample. The presence of thorium in the cake dissolution samples causes a precipitate of thorium iodate when HIO_4 is used which interferes with the colorimeter readings.

Reagents and Apparatus

1. Oxidation solution, ammonium persulfate, saturated.
2. 1.0 M $AgNO_3$
3. Klett colorimeter, 540-m μ filter

Procedure

1. Pipet exactly 2.0 ml of the oxidizing solution into two flat-bottomed 2-ml Klett colorimeter tubes.
2. Add 25 λ 1.0 M AgNO_3 .
3. Place tube in hot water bath and allow to heat to 80° to 90°C. Add sample to one tube and carry the other tube through the procedure as a blank.
4. Continue heating until color production appears complete and then cool to room temperature in a cold water bath.
5. Place the microtube adapter on the Klett colorimeter and push in the adapter compensator knob on the left side of the colorimeter.
6. With the 540-m μ filter, balance the instrument at 0 on the reagent blank, and then read the optical density of the sample.*
7. Obtain the number of micromoles of manganese by dividing the Klett reading by 575 (1 μ mole manganese reads 575).
8. Calculations:

$$\underline{\mu \text{ Mn}} = \frac{\mu \text{ moles of Mn}}{\lambda \text{ of sample}}$$

9. A standard is run daily.

Phosphate Ion (Colorimetric)

Principle of Method

Phosphate is added in the LAF to lower the extraction coefficient of protactinium with TBP under LA bank extraction conditions. It is conveniently determined by the molybdenum blue colorimetric method.⁽²⁹⁾ Nitrates interfere but are removed by fuming with perchloric acid.

Reagents and Apparatus

1. 10% Na_2SO_3
2. 0.15% Hydrazine sulfate
3. 2% $(\text{NH}_4)_2\text{MoO}_4$ in 11 N H_2SO_4
4. Ammonium molybdate - hydrazine sulfate reagent. Dilute 25 ml $(\text{NH}_4)_2\text{MoO}_4$ solution to 90 ml with distilled water, add 10 ml hydrazine sulfate solution, and mix well. This mixture is not stable and should be mixed only as needed.
5. Phosphate standard (3 μg phosphate/ml)
6. HClO_4 , conc
7. Klett colorimeter with 660-m μ filter and 4-cm cells
8. 50-ml beakers
9. 50-ml volumetric flasks

*It should be noted that the flat-bottomed (2-ml) colorimeter tubes must rest on top of the spring stop so that the 2-ml samples will cover the window of the microtube adapter.

Procedure

1. Place sample in 50-ml beaker, add 3 ml HClO_4 , and heat to white fumes (not dryness).
2. Cool, add water, and dilute to 10 ml.
3. To two other 50-ml beakers, add 10 ml of the phosphate standard, and 10 ml distilled water, respectively. These three beakers are then run simultaneously, one as the sample, another a standard, and the third a reagent blank.
4. Add 3 ml HClO_4 and 15 ml 10% Na_2SO_3 to each solution.
5. Heat in boiling water bath for a few minutes to bring them near the boiling point. Add 20 ml of ammonium molybdate - hydrazine sulfate reagent. (See No. 4 under Reagents and Apparatus.)
6. Heat in boiling water bath for 15 min.
7. Cool rapidly by holding each flask under cold running water and dilute to mark on the 50-ml volumetric flask with distilled water.
8. Read on the Klett-Summerson colorimeter against distilled water at 660μ . Subtract the blank reading of optical density from the standard and sample readings. Calculate the micrograms phosphate by dividing the sample reading by the reading equivalent to 1 μg phosphate (one-thirtieth the 30 μg standard reading). Then

$$\text{ppm PO}_4^{-3} = \frac{\mu\text{g phosphate}}{\text{ml sample}} = \frac{\text{optical density}}{(\text{ml sample})(\text{optical density } \mu\text{g PO}_4^{-3} \text{ standard})}$$

NOTE: The blank should read very low (< 10). Recovery of the standard should be $100 \pm 10\%$. High blanks are usually caused by the use of glassware which has previously been cleaned with calgon- or phosphate-containing soaps. Extreme care should thus be taken to keep this glassware separate and it should be cleaned with sulfuric and chromic acid cleaning solution only.

Per Cent Tributyl Phosphate (Density Method)

Principle of Method

When a solution is made up of two liquids of widely separated densities, the density of the solution serves as a convenient measure of its composition, provided the volumes are additive. The volume per cent of tributyl phosphate in Amsco 123-15 or Ultrasene is found by this method. The method is sensitive to the density of the diluent and to temperature. A reduction of 0.001 in the density of diluent causes an apparent decrease in TBP content of 0.4% at 30% TBP. Every degree increase in temperature over 25°C causes an apparent decrease in TBP content of 0.4% at 30% TBP. A value of 0.779 is used for Amsco 123-15 or Ultrasene and all drums to date have ranged from 0.777 to 0.779. The method has been found to be the most rapid method for TBP determination.

Apparatus

1. Constant temperature bath held at $25 \pm 0.1^\circ\text{C}$.
2. Special hydrometer, (8) constructed so that there is a difference of 0.07 in. (about 1/16 in.) on the stem for each 0.1% TBP in the region of 28 to 32% TBP. The hydrometer is constructed of glass and weighted with paraffin and sand to float at the proper depth in a known 30% TBP solution; the top is then flamed closed. It is designed for a 250-ml graduated cylinder and is read to 0.1% TBP.

Procedure

1. Place 150 ml of the sample and the special hydrometer in a 250-ml graduated cylinder in a constant temperature water bath at $25 \pm 0.1^\circ\text{C}$. Allow to attain temperature equilibrium.
2. Spin the hydrometer slightly between the fingers so that it will center in the liquid. Do not take a reading while the hydrometer is touching the side of the cylinder.
3. Read the per cent TBP from the hydrometer by sighting directly across the underside of the air-liquid interface.
4. If the density is determined by a pycnometer, the per cent of TBP can be calculated from the following equation:

$$\% \text{ TBP} = \frac{(D \text{ sample} - D \text{ diluent}) + 0.0002^*}{(D \text{ of TBP} - D \text{ diluent})} \times 100$$

Per Cent Tributyl Phosphate (Dielectric Method)

Principle of Method

Tributyl phosphate and the hydrocarbon diluent have different dielectric constants (TBP is near 8, the hydrocarbon 2). A measure of the dielectric property of the two-component mixture serves as a measure of composition. The samples must be pretreated to remove foreign constituents (acid, uranium, thorium, DBP, etc.) and to add a constant amount of water. The ORNL Model Q-946 instrument⁽³⁰⁾ has been adjusted to read only from 28 to 37% TBP for a 360° turn of the dial. The dial can thus be read to 0.1%. This method is one of the more accurate methods for TBP analysis.

Apparatus

1. Dielectric constant meter, ORNL Model Q-946.

*Nonlinearity correction for 25 to 35% TBP.

Procedure

1. Place about 50 ml of the sample in a separatory funnel. Add an equal volume of 2% Na_2CO_3 solution, and shake thoroughly. Discard the aqueous layer. Contact twice more with fresh equal portions of distilled water. After discarding the final water layer, centrifuge the organic phase to remove all traces of excess water.
2. Pour the sample into a clean, dry 50-ml beaker. Into two other beakers place 29% and 31% TBP standard solutions which have previously been treated as in Step 1.
3. Clean the condenser probe with acetone and air dry, then place it in the 29% and 31% standard TBP solutions, cleaning the probe between readings.
4. Plot the dial readings for maximum deflection of the micro-ammeter vs per cent TBP and draw a straight line through the two points.
5. Clean the probe as before and place it in the unknown sample. Obtain the dial reading for maximum deflection of the micro-ammeter.
6. Read the per cent TBP from the calibration curve.

Unstable Constituents in Tributyl Phosphate Diluent⁽³¹⁾

Principle of Method

The diluent for TBP should be free of acids, alkalis, suspended materials, olefins, and the various aromatics, since these contaminants lower the extraction efficiency or decontamination factors available from the process. Thus, the diluent is preconditioned by various washing procedures. A test for the effectiveness of pretreatment is the reactivity to chromyl chloride, which will oxidize double bonds as well as aromatic components, both of which are the most difficult of contaminants to remove. The analysis results from a time-rate study where the unconsumed Cr^{+6} is suddenly quenched with Fe^{++} . Extrapolation to zero time gives the difference between added and consumed Cr^{+6} and thus the unstability equivalent.

Apparatus and Reagents

1. 10-ml burette.
2. 0.2 N standard ferrous sulfate
3. 1.0 N standard chromyl chloride in carbon tetrachloride.
4. 1.0 N standard sodium dichromate
5. 0.005 M ferroin indicator (orthophenanthroline ferrous sulfate).
6. 6 N H_2SO_4

Procedure

1. Into each of five 125-ml iodine flasks, pipet 1 or 2 ml of a standardized chromyl chloride solution.
2. 1.0 ml of the hydrocarbon diluent whose unstableness is to be tested is carefully layered on the surface of the CrO_2Cl_2 .
3. Shake tubes essentially together, and term this time as "0" time.
4. Stop the reaction by addition of 5 ml of 6 N H_2SO_4 followed by 5 ml of standard FeSO_4 at time intervals such as 10, 20, 30, 60, and 90 min.
5. Titrate the samples potentiometrically for excess Fe^{++} with standard $\text{Cr}_2\text{O}_7^{=}$ with Pt - calomel electrodes or titrate to the ferroin end point (disappearance of red iron complex).
6. Plot data on semilog graph paper, the Cr^{+6} equivalents remaining vs time. Extrapolate to "0" time to find milliequivalents Cr^{+6} . Subtract this figure from the initial Cr^{+6} equivalents initially added to give the degree of unstability.

Calculations

1. $(\text{ml} \times \text{N } \text{FeSO}_4 \text{ added}) - (\text{ml} \times \text{N } \text{Cr}_2\text{O}_7^{=}) = \text{milliequivalents } \text{CrO}_2^{++} \text{ remaining}$
2.
$$\frac{\text{Meq. } \text{CrO}_2^{++} \text{ added} - \text{extrap. Meq. } \text{CrO}_2^{++}}{\text{Diluent sample size in ml}} = \text{N unstability}$$

APPENDIXES

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APPENDIX 1

Determination of Free Acid in the Presence of
Thorium and Uranium (Conductometric)

A conductometric method for the determination of free hydrogen ion in the presence of hydrolyzable ions has been described,⁽³²⁾ and this technique has been applied to the determination of free acidity in thorium solutions.⁽¹²⁾

Fluoride complexes thorium as ThF_2^{++} or as addition compounds such as $\text{ThF}_4 \cdot \text{HF}$ and $\text{ThF}_4 \cdot 2\text{HF}$. The first complex is unsatisfactory for subsequent acid titration because of the uncertainty in stoichiometrically forming ThF_2^{++} . The addition compounds cannot be used since the subsequent titration becomes one of the weak acid - strong base type with an indeterminate end point.

The difficulty was resolved by quantitatively precipitating thorium as ThF_4 using NaF and alizarin to indicate the end point. The conductometric acid base titration was then made in the same solution. Recoveries ranged from 98%, where the ratio of thorium to acid was 7.5, and 85% at a ratio of 25.

APPENDIX 2

Separation and Determination of Thorium and Aluminum(33)

Thorium was found to be quantitatively extracted into mesityl oxide from solutions nearly saturated with LiNO_3 , while incomplete extractions were obtained from solutions saturated with NaNO_3 .

A simple, rapid, and accurate method of measuring the extracted thorium which had been stripped into distilled water was accomplished by a spectrophotometric titration of ethylenediamine tetra-acetic acid (EDTA). An initial titration with a standard thorium solution produced a calibration curve used on all "unknowns."

Briefly, the method consists of adding the unknown amount of backstripped thorium to a flask containing the same quantities of EDTA and indicator as were present in the initial titration, and then titrating to a point beyond the end point with the standard thorium solution. From the total thorium present and the volume of the standard solution added, the unknown thorium content of the sample is determined. This method requires only one standard solution, only one initial pH adjustment, and the measurement of a single absorbance for each thorium determination.

Aluminum can be quantitatively precipitated from the original aqueous phase with 8-quinolinol subsequent to the extraction of thorium.

APPENDIX 3

Chromatographic Separation of Monobutyl Phosphate
and Dibutyl Phosphate

Chromatography offers a convenient means of separating substances of similar structure and properties. Some work was done on the separation of dibutyl phosphate from monobutyl phosphate on a qualitative basis using the scheme of Hanes and Isherwood.⁽³⁴⁾ Strips of Whatman No. 1 paper were washed with 0.1 M HCl and distilled water and spotted with solutions and mixtures of ca. 0.01 M MBP and DBP. The strips were equilibrated in a tank with a mixture of 60 ml ethanol, 30 ml NH_4OH (conc), and 10 ml distilled water, and then developed with the solvents for about 7 to 10 hours (solvent front moved 20 to 30 cm). The papers were then dried (short oven heating at 85°C) and the strips sprayed with a spot testing solution containing 1% $(\text{NH}_4)_2\text{MoO}_4$, 5% HClO_4 , and 1% HCl. Hydrolysis of the esters was followed by heating and the characteristic molybdenum blue color appeared.

The chromatogram of MBP showed a distinct spot which was centered in the strip and was followed by a distinct band which spread across the strip. There was no tailing, thus indicating effective separation. The R_f values (ratio of spot movement to total solvent front movement) of the two markings were 0.43 and 0.68.

The chromatogram of DBP showed only one band spread across the strip at an R_f value of 0.90 to 0.92.

A mixture of MBP and DBP resulted in three markings with R_f values of 0.48, 0.69, and 0.91, respectively, an indication that the separation is real and can easily be observed.

No attempts have yet been made to adapt this technique to the quantitative estimation of either constituent in the presence of the other. Presumably some type of elution technique could be used whereby that portion of the strip known to contain only one of the mixture of constituents could be quantitatively eluted, then given a standard phosphate analysis. The use of tracer techniques coupled with the production of a soluble metal complex which would still give differing R_f values might be applied. Standard counting techniques could be used on the strip directly.

An irradiated 30% TBP sample was "chromatized" and developed for evidence of DBP formation. A very faint band was obtained at an R_f value about 0.86 to 0.90. A DBP analysis indicated 1476 ppm DBP. Difficulty was encountered in drying the strip after sampling and before developing. A very large area on the paper was wet by 30% TBP.

APPENDIX 4

Additional Problems

Following is a list of studies which were under consideration or in progress when the KAPL Thorex program closed. Their solution would aid materially in discussing more critically the results obtained from the Thorex process while experimental flow sheets are being devised.

1. Development of an accurate method for determination of U-233 in LAF.

This is important for the determination of conversion or grams U-233/ton thorium. A direct count results in counting also the α 's in the decay chain of Th-228. Although they are in small percentage compared to U-233 α 's, a correction factor must still be applied to the LAF gross α count when calculations are made. Typical gross α distribution⁽¹³⁾ in irradiated thorium is U-233 74.9%, Ra-224 11.6%, U-232 8.1%, Th-228 2.9%, U-234 2.3%, Th-232 0.2%.

2. Development of a method for the determination of Th-228 in the presence of ruthenium, zirconium and cerium.

The unique determination of Th-228 is very important because it is the major activity which limits the df obtainable by solvent extraction techniques. Further study on the determination of UX (Th-234) by mesityl oxide extraction (page 35) might result in obtaining Th-228 also. All the thorium isotopes (Th-228, -232, -234) will extract. Th-234 is counted directly for beta activity. After a period of time (about 2 weeks) equilibrium between Th-228 and its daughters Bi-212, Pb-212 should be established. The strong gamma ray (1.80 Mev) from Bi-212 may then be separated from other gamma activities by gamma scintillation spectrometry with single or multichannel analyzers, and thus Th-228 can be measured.

3. Development of a method for the determination of Ra-224 in the presence of thorium, uranium, and fission products.

Since Ra-224 is one of the daughters in the decay chain of Th-228, the analysis of Ra-224 would also give a measure of the limiting df obtainable on solvent extraction. A radiochemical method might be developed with BaSO₄ as carrier.

4. Development of a method for determining Bi-212 and Tl-208.

5. Development of a method for determining aluminum in LAF.
The titrimetric method described by Bank and Edwards (33) might be modified to use on small aliquots of the highly radioactive feed solution.
6. Modification of the PO_4^{-3} procedure to avoid NO_3^- interference without fuming and decomposition of MBP and DBP by use of sulfuric acid solvent extraction of phosphomolybdate or by ion exchange.
7. Further study of the analysis of $\text{Th}(\text{DBP})_x$ or $\text{Th}(\text{MBP})_x$ precipitates by thermogravimetric balance and carbon-hydrogen analyses.
8. Consideration of the effectiveness of the refractive index for the determination of LBT composition.
9. Redetermination of the absolute counting efficiency of the spectrometer with change in gamma energy to facilitate absolute fission-product analysis.
10. Development of a more satisfactory Pa-233 analysis (possibly chromatography).

APPENDIX 5

Solvent Washing Procedure

After analyses were complete on the 1CW composite streams from a flow sheet test, they were all combined. The solvent was washed in the control laboratory for further use by the miniature mixer settler units according to the following procedure:

1. A wet mount of the solvent was made on filter paper pulp and the plate was counted for gross β , γ activities, and Ru- γ and Nb-Zr γ at their respective photopeaks on the gamma scintillation spectrometer.
2. First wash: Mix the 30% TBP with 1/10 its volume of distilled water for 15 min in a 1-liter separatory funnel. Allow the phases to separate for 15 min before drawing the aqueous phase off.
3. Second wash: Mix the 30% TBP with 1/10 its volume of 0.1 M NaOH for 1 hr. Allow 15 min for phase separation. Discard aqueous phase.
4. Third wash: Repeat first wash.
5. Fourth wash: Mix the 30% TBP with 1/10 its volume of 0.05 M HNO_3 for 15 min. Allow 15 min for the phases to separate and discard the aqueous phase.
6. Mount 2.0 ml of the 30% TBP and count in the same manner as in Step 1. Decontamination factors are on the order of 20 to 40 for gross β and γ .

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APPENDIX 6

Table of Sample Sizes for Thorex Streams

	<u>H⁺</u>	<u>Th</u>	<u>α</u>	<u>β-γ</u>	<u>Zr-Nb</u>	<u>Cs-γ</u>	<u>UX(β)</u>	<u>TRE</u>	<u>Pa</u>	<u>TRE+UX</u>
Head End and 1AF	50 λ KOX	FD	1.0 ml x 1000	20-100 λ x 1000	β - γ Mount. Spect.	500 λ x 1000 TPB	-	-	β - γ Mount. Spect.	20 λ x 1000
1 AW	100 λ KOX	10 λ Thoron	-	-	-	-	-	-	-	-
1 CU Composite	2.0 ml MR	-	10 λ DM	4.0 ml DM	β - γ Mount. Spect.	-	4.0 ml IO ₃	4.0 ml IO ₃ -OX	β - γ Mount. Spect.	-
1 BT Composite	500 λ KOX	FD	100 λ HEX	2.0 ml DM	β - γ Mount. Spect.	-	100 λ IO ₃ or MO	4.0 ml IO ₃ -OX	β - γ Mount. Spect.	-
1 CW Composite	-	-	1.0 ml DM	1.0 ml DM	β - γ Mount. Spect.	-	-	-	-	-

KOX Potassium Oxalate Method
 FD Falling Drop
 Spect. Gamma Counted on Scintillation Spectrometer
 Thoron Thoron Colorimetric Method
 MR Titration Method using Methyl Red Indicator
 IO₃ Zirconium Iodate Precipitation Method
 IO₃-OX Zirconium Iodate Followed by Oxalate for Mounting
 HEX Hexone Extraction Method for U-233
 DM Direct Mount
 MO Mesityl Oxide Extraction Method for Th-234

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APPENDIX 7

Heating Block for Organic Mounts

Organic liquids will wet stainless steel plates to such an extent that during evaporation the sample has a tendency to spread and creep underneath the plate. This has been remedied somewhat by use of a specially constructed heater which consists of an aluminum block about 4 in. in diameter and 1 in. thick with a hole 0.5 in. in diameter running through the center. The block is heated by placing it on a 4-in. Chromalox ring heater. The plate on which the solution is to evaporate is placed in a depression on the upper face. To keep the solution in the center of the plate a fine stream of cold air is blown through the center from the bottom of the block. Thus the plate is heated from the periphery, and the heat tends to travel from the outer edges to the center. If the temperature gradient between the edges of the plate and the center is large enough, the solution will have a tendency to remain in the center until it has evaporated to dryness.

Block temperature is important. TBP in Ultracene mounts best at 225°C. Care must be taken to prevent boiling of the solution being mounted because of spattering problems.

The most suitable thermometers are available from the A. H. Thomas Company. They are 3 in. long, with a range from 0 to 300°C.

Volumes up to 500 λ can be mounted very conveniently. In mounting large samples the first addition should evaporate nearly to dryness before more sample is added.

APPENDIX 8

Fission-Product Filtrator

Fission-product precipitates are conveniently mounted by use of a filtrator device.⁽⁸⁾ The lower half of the device is made from a 20-mm-diam sealing tube with a medium glass frit. The tube is cut and ground flush with the frit. A disk of filter paper is placed on the frit, and a chimney is fastened in place over the paper. Solutions to be filtered are poured in the chimney while a vacuum from a suction flask is drawn from below.

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Many of the methods described herein are also reported in the following reports:

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- KAPL-348 "Methods of Chemical Analysis for Separations Process Research Unit. Part II. Radiochemical Methods," by J. F. Flagg, B. F. Rider, and W. S. Andrus, July 7, 1950. (Confidential Reference)
- KAPL-572 "Analytical Control Methods for Purex," by B. F. Rider, April 27, 1951. (Secret Reference)
- KAPL-1264 "Analytical Chemical Methods for Zirconium-Niobium Isolation Pilot Plant," by B. F. Rider, M. E. Jones, and Mrs. H. C. Hendrickson, February 27, 1956. (Confidential Reference)

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