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**MOUND LABORATORY CHEMISTRY AND PHYSICS PROGRESS REPORT:
JULY-SEPTEMBER 1969**

AEC Research and Development REPORT

MONSANTO RESEARCH CORPORATION

A S U B S I D I A R Y O F M O N S A N T O C O M P A N Y

M O U N D L A B O R A T O R Y

MIAMISBURG, OHIO

OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

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**MOUND LABORATORY CHEMISTRY AND PHYSICS PROGRESS REPORT:
JULY-SEPTEMBER 1969**

Issued: February 9, 1970

MONSANTO RESEARCH CORPORATION

A Subsidiary of Monsanto Company

MOUND LABORATORY

Miamisburg, Ohio

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Foreword

The Mound Laboratory Chemistry and Physics Progress Report, issued quarterly, is intended to be a means of reporting items of current technical interest in research and development programs. Since this is an informal progress report, the results and data presented are preliminary and subject to change.

These reports are not intended to constitute publication in any sense of the word. Final results either will be submitted for publication in regular professional journals or will be published in the form of MLM topical reports. Questions concerning the material compiled here should be directed to G. R. Grove, Director, Nuclear Operations.

Previous reports in this series are:

MLM-1606	MLM-1520
MLM-1603	MLM-1494
MLM-1531	MLM-1456
MLM-1526	MLM-1443

Summary

RADIOCHEMISTRY

Alpha-Beta Branching Ratio of Actinium-227 The alpha branching ratio of ^{227}Ac has been determined by two independent methods. The intermediate means from the two methods were in good agreement: $(1.3802 \pm 0.0069)\%$ and $(1.3799 \pm 0.0045)\%$. The weighted grand mean from 12 determinations was $(1.3800 \pm 0.0036)\%$. A computational technique was developed and tested which is believed to be useful as a non-destructive analytical tool for the determination of ^{227}Ac by alpha spectrometry in the presence of interfering decay products. (Page 6)

INORGANIC CHEMISTRY

Stability of Hydridic Rare Earth Compounds A new method of preparing fluorite-type oxide hydrides of gadolinium has been found. The compounds can be prepared by dissolving gadolinium metal in warm, aqueous sodium hypochlorite or in acids such as acetic, propionic or propiolic. Some observations on the chemical stability of these compounds are presented. (Page 24)

SEPARATION CHEMISTRY

Uranium-234 Recovery New facilities for the recovery of uranium-234 from waste plutonium-238 anion exchange raffinates are in operation. The process includes extraction of the uranium with tri-n-octyl phosphine oxide, stripping from the organic phase, and purification by anion exchange. Minor problems were encountered in the start-up, the main one being that of analysis of various intermediate process solutions. A total of 3.23 g of uranium-234 has been recovered and purified in the new facilities. (Page 26)

Thorium-229 Recovery Analytical work on the 42 drums of NFS raffinate was concluded and the presence of large quantities of thorium-232 was confirmed. Because of this result, plans for future recovery of the thorium content are indefinite.

During this period, 1.6 mg of thorium-229 were separated and shipped from 39 g of the 11-yr-old uranium-233 "cow" on hand. (Page 35)

ANALYTICAL CHEMISTRY

Analysis of the Sixth Cooperative Boron Samples and High Purity Boron

Several different analytical techniques were used to determine the total boron content and the impurity levels of a number of boron samples. Good agreement was obtained for impurity determinations between atomic absorption spectrophotometry and emission spectroscopy. (Page 37)

Infrared Analysis of Water in 2-Ethyl-1-Hexanol A spectrophotometric technique is being tested for analysis of the water content of 2-ethyl-1-hexanol. The absorbance measured at 1925 μ on a series of samples gave a straight line when plotted as a function of water concentration. (Page 39)

Spectrophotometric Determination of Thorium in the Presence of Uranium Using Arsenazo-III A method for determining trace quantities of thorium in samples containing uranium is being developed. Investigation revealed that up to four times as much uranium as thorium in a sample did not considerably affect the thorium analysis. In addition, small amounts of nitric acid and aluminum caused little interference. (Page 40)

Structure Determination of Calcium Tellurate with X-Ray Powder Diffraction Data X-ray diffraction techniques are being used to determine the lattice parameters and crystal structure of calcium tellurate. Film data and corrected diffractometer data were used to compute three-dimensional Patterson functions for the compound. The compound can be considered isomorphous with calcium uranate because of the similarity between the diffraction diagrams of the two materials. (Page 42)

Thorium Determination Formation of the thorium-thorin complex and measurement at 545 μ provides a means for rapidly determining up to 80 μ g of thorium in the presence of plutonium. Good precision was also possible when the EDTA indirect titration of thorium was used on thorium solutions which had been purified of the plutonium interference. (Page 45)

Radiochemistry

ALPHA-BETA BRANCHING RATIO OF ACTINIUM-227

The entire question of the branching ratio of actinium-227 has been reopened and an independent method has been developed to complement and test the absolute accuracy of the method previously described.¹ Inasmuch as substantial changes have been made in the original computational technique (chiefly in the method of correcting for tailing of ^{227}Th), both methods are described in detail in the following pages.

Actinium-227 decays primarily by beta emission, but its maximum beta energy is only 46 keV. In the present state of the art of nuclear spectrometry, the beta decay of ^{227}Ac is virtually useless for analytical purposes because of the abundance of beta-emitters in the decay chain (Figure 1).

A small fraction of the decay of ^{227}Ac is by alpha emission, yielding ^{223}Fr , a beta-emitter. However, the exact value of the alpha-beta branching ratio is in doubt; it was reported to be about 1% by Mlle. Perey, the discoverer of francium² and $(1.25 \pm 0.02)\%$ by Peterson and Ghiorso.³ More recently, Nurmi et al.⁴ found the ratio to be $(1.45 \pm 0.06)\%$. This value was based on the early growth of ^{227}Th into a freshly purified source of ^{227}Ac ; unfortunately, the ^{227}Th half-life of 18.2 days,⁵ which was used in computing the growth rate, is incorrect. Highly precise calorimetric measurements have shown that the half-life of ^{227}Th is 18.7176 ± 0.0052 days.⁶

All methods for the absolute determination of ^{227}Ac by means of its radioactivity depend ultimately on an accurate knowledge of its alpha-beta branching ratio. Obviously, a significant error in that ratio affects the validity of any microanalytical result, whether derived from the separation and counting of ^{223}Fr ,^{7,8} the direct spectrometric measurement of the 4.94-MeV alpha emission⁹ or the growth of decay products.¹⁰ (However, in calorimetric determinations of macroscopic amounts of ^{227}Ac , the ratio is relatively insignificant, since heat measurements do not differentiate between alpha- and beta-decay.)

FIGURE 1 - The ^{227}Ac decay chain.

Experimental

Chemical Separations The ^{227}Ac equilibrium mixture (AEM), as well as all reagents, equipment and techniques, were the same as those previously described.¹¹

Two types of separation were performed:

- A. A sample of AEM was deposited on a platinum disk, dried, converted to the fluoride form with 1N HF, and leached with 0.01N HF. The disk was ignited at red heat. This separation produced a source containing ^{227}Ac and ^{227}Th in secular equilibrium, but essentially free of ^{223}Ra and its decay products (Figure 2).
- B. A sample of AEM was deposited on a platinum disk, dried, metathesized with 0.1N NH_4NO_3 , and heated at 200°C for 5 min. The residue was leached with 0.1N NH_4NO_3 and the desorbate (containing the ^{227}Ac and ^{223}Ra) was transferred to a second platinum disk. The first disk (containing the ^{227}Th) was discarded. The residue on the second disk was dried, covered with 3N NH_4OH , dried again and heated at 200°C for 5 min. The disk was cooled

FIGURE 2 - Alpha spectrum of ^{227}Ac source prepared by method A.

to 98°C, leached with 0.02N NH_4NO_3 /3N NH_4OH , and the desorbate (containing the ^{223}Ra) was discarded. The time of this desorption, when the ^{227}Ac was essentially free of decay products, was noted as T_0 , the separation time. The second disk was heated at 200°C for 5 min, but not ignited. This type of separation yielded the spectrum shown in Figure 3.

Alpha Spectrometry The spectrometer system consisted of an ORTEC detector-amplifier, including a 100-mm² silicon surface barrier detector (Model 100-60), a detector bias supply (Model 210), a preamplifier (Model 109A), a linear amplifier (Model 410) and a biased amplifier (Model 408). The amplifier output was fed to a Nuclear Chicago 400-channel pulse height analyzer (Model 34-27) equipped with a digital magnetic tape recorder (Model 52-35). An IBM 360/50 computer was used to analyze the data.

The system was adjusted for an energy range of 3.8 to 7.8 MeV and the source was placed in the detector chamber. After the chamber was evacuated and bias voltage was applied, the source and the detector-amplifier system were left undisturbed for the duration of the experiment.

Each tape cartridge contained enough magnetic tape to record up to 40 spectra. The analyzer was programmed to store data for a selected period of time (usually 60 min), read out the data to the magnetic tape recorder, erase the spectrum stored in the memory, and repeat the cycle indefinitely or until the available tape storage was exhausted.

Since each experiment lasted for several days or weeks, some spectral drift was expected. Therefore, each recorded spectrum was calibrated individually by the computer. The calibration was based on the 4.944-MeV (composite) peak of ^{227}Ac and the 7.384-MeV peak of ^{215}Po . Linearity was checked in each spectrum by computing the location of the 6.036-MeV peak of ^{227}Th ; the observed and computed peak locations always agreed within one channel number. Resolution, based on the isolated ^{215}Po peak at 7.384 MeV, was 20-25 keV (full width at half maximum height corrected to 5.477 MeV).

Theory

The Alpha Spectrum of ^{227}Ac Although the principal alpha peaks of ^{227}Ac are readily discernible in a well-resolved spectrum any quantitative estimate of the area under those peaks is likely to be high because of "tailing" of the more energetic alpha particles of its decay products (Figure 4). The tailing problem exists in any mixture of alpha-emitting nuclides, but it is particularly significant in the case of ^{227}Ac because of its relatively low specific alpha activity and the abundance of higher-energy alpha-emitters in the decay chain.

Tailing interference is due primarily to energy degradation within the source and the detector window. However, additional interference comes from ^{219}Rn nuclei ejected from the source by alpha recoil. These nuclei may decay anywhere within the detector vacuum chamber, so that some of

FIGURE 3 - Alpha spectrum of ^{227}Ac prepared by method B.

FIGURE 4 - Alpha spectrum of ^{227}Ac in equilibrium with its decay products.

the alpha particles resulting from the decay of ^{219}Rn and its daughters reach the window from random distances and at random angles, producing further distortion of the ^{227}Ac spectral region.

The magnitude of the interference is materially reduced (but not eliminated) when ^{223}Ra and its decay products are removed (Figure 2). Separation of ^{227}Ac from all decay products affords temporary relief from interference (Figure 3), but the spectrum is soon distorted by the formation of new decay products. In a typical case, the counting rate between 4.1 and 5.1 MeV of a freshly purified ^{227}Ac source increased by 7% within 18 hr; after 162 hr the counting rate in the same spectral region had increased by 38%.

In order to achieve good precision of ^{227}Ac counting rates, long counting intervals are necessary. However, while longer intervals yield higher precision, accuracy is reduced by increased interference from the rapidly growing decay products. Correction for this systematic error can be made by analysis of a series of spectra if it is assumed that the magnitude of the interference is a linear function of the alpha activity above 5.0 MeV, the upper limit of the ^{227}Ac spectral region.¹² The two methods to be described are based on this assumption.

Analysis of Sources Prepared by Method A The basic assumption of method A is that only ^{223}Ra and its decay products are removed; losses of ^{227}Ac and ^{227}Th , if any, are assumed to have been mechanical and apply equally to both nuclides. That is, ^{227}Th remains in equilibrium with ^{227}Ac and is, therefore, constant. Assuming, further, that the alpha counting efficiency, c , is the same for ^{227}Ac and ^{227}Th and that the decay constant of ^{227}Ac is negligible as compared with that of ^{227}Th ,

$$\left. \begin{aligned} \text{Ac}^* &= cN_0\lambda_1 B \\ \text{Th}^* &= cN_0\lambda_1 (1 - B) \\ \text{D}^* &= \text{Ac}^* + \text{Th}^* = cN_0\lambda_1 \end{aligned} \right\} \quad (1)$$

where $N_0\lambda_1$ is the disintegration rate of ^{227}Ac , B is the fraction which decays by alpha emission (i.e., the branching ratio), Ac^* is the effective alpha disintegration rate of ^{227}Ac , Th^* is that of ^{227}Th , and D^* is the effective disintegration rate of ^{227}Ac by both alpha and beta decay.

The alpha energies of ^{227}Th fall between 5.032 and 6.037 MeV¹³ and those of ^{223}Ra fall between 5.102 and 5.870 MeV.¹⁴ It would appear, at first glance, from the genetic relationships and half-lives given in Figure 1, that correction for alpha counts due to residual or growing ^{223}Ra in the ^{227}Th region could be made simply by subtracting the counting rate of ^{215}Po from the apparent counting rate of ^{227}Th . This assumption was made by Nurmia,⁴ but it is only approximately valid.

Depending upon the physical characteristics of the source, recoil losses of ^{215}Po may be substantial. While these losses can be minimized by ignition of the source, they cannot be entirely eliminated unless the source is hermetically sealed.¹⁵ However, if a series of alpha spectra is obtained as the ^{223}Ra grows back towards equilibrium over a period of several days or weeks, the ratio of ^{215}Po counts to ^{223}Ra counts in a given spectral region will remain constant. That is:

$$\left. \begin{aligned} \text{Th} &= \text{Th}^* + r\text{Po} \\ \text{D} &= \text{D}^* + q\text{Po} \end{aligned} \right\} \quad (2)$$

where Th is the observed counting rate in the ^{227}Th spectral region and r is the ratio of ^{223}Ra in that region to Po, the observed counting rate of ^{215}Po . D and q have analogous meanings with respect to D*. The validity of Equations 2 is illustrated by the results reported in Table 1.

Superficial treatment of the data in Table 1 would suggest a branching ratio of 2.5%, if it were assumed that tailing of ^{227}Th is negligible below 5.1 MeV. Fewer than 0.08% of the ^{227}Th alpha particles have energies lower than 5.58 MeV,¹³ and tailing below 5.10 MeV is a relatively insignificant fraction of the total ^{227}Th alpha decay. However, because of the low specific alpha activity of ^{227}Ac , tailing by ^{227}Th is a large fraction of the total alpha activity below 5.10 MeV.

Since this problem has a bearing on the more general one of determining ^{227}Ac by alpha spectrometry in the presence of its decay products, the mathematical treatment is given in some detail. The imaginary alpha spectrum in Figure 5 will be used as a model for the following derivation:

Consider a spectrum containing alpha peaks in channels x_1 , x_2 and x_3 , with peak heights Y_1 , Y_2 and Y_3 , respectively. Assume that the low-energy side of peak 3 is adequately represented by

$$y_3 = Y_3 e^{-h_3(x_3 - x)} = C_3 e^{h_3 x}$$

where y_3 is the count due to Y_3 in any channel, $x < x_3$, h_3 is a constant which is inversely proportional to the resolution at x_3 , and

$$C_3 = Y_3 e^{-h_3 x_3}$$

The equation describing peak 2 will then be:

$$y_2 = (Y_2 - C_3 e^{h_3 x_2}) e^{-h_2(x_2 - x)} + C_3 e^{h_3 x}$$

and, for peak 1:

$$y_1 = C_1 e^{h_1 x} + C_2 e^{h_2 x} + C_3 e^{h_3 x}$$

Table 1

COUNTING RATES CORRECTED FOR ^{223}Ra INTERFERENCE AS A FUNCTION OF TIME FOR SOURCE 401325

Time Span (hr)	Number of Spectra	Th* (5.11 - 6.20 MeV)		D* (4.10 - 6.20 MeV)	
		counts/hr	r ^a	counts/hr	q ^a
45	22	62555 ± 271	1.149 ± 0.032	64171 ± 274	1.181 ± 0.032
59	32	63068 ± 201	1.087 ± 0.022	64622 ± 207	1.126 ± 0.022
98	56	62860 ± 96	1.110 ± 0.008	64380 ± 97	1.153 ± 0.008
134	91	62876 ± 67	1.109 ± 0.004	64419 ± 67	1.150 ± 0.004
192	114	62935 ± 52	1.105 ± 0.003	64478 ± 52	1.145 ± 0.003
209	134	62934 ± 47	1.105 ± 0.002	64476 ± 48	1.145 ± 0.002
236	156	62902 ± 44	1.107 ± 0.002	64441 ± 44	1.148 ± 0.002
254	175	62942 ± 42	1.105 ± 0.002	64480 ± 42	1.145 ± 0.002
300	214	62905 ± 40	1.106 ± 0.001	64445 ± 40	1.147 ± 0.001
360	235	62879 ± 40	1.108 ± 0.001	64418 ± 40	1.149 ± 0.001
376	257	62866 ± 40	1.108 ± 0.001	64404 ± 40	1.149 ± 0.001
418	297	62815 ± 39	1.111 ± 0.001	64355 ± 39	1.152 ± 0.001
466	336	62831 ± 37	1.110 ± 0.001	64370 ± 37	1.151 ± 0.001
800	373	62902 ± 35	1.108 ± 0.001	64473 ± 35	1.147 ± 0.001

^aThe symbols r and q represent the ratios of ^{223}Ra to ^{215}Po in the indicated energy regions as computed by Equations 2.

FIGURE 5 - Alpha spectrum model.

where:

$$C_2 = (Y_2 - C_3 e^{h_3 x_2}) e^{-h_2 x_2}$$

and

$$C_1 = (Y_1 - C_2 e^{h_2 x_1} - C_3 e^{h_3 x_1}) e^{-h_1 x_1}$$

For the general case of a spectrum containing n peaks:

$$y = \sum_{i=1}^n C_i e^{h_i x} \quad (3)$$

where:

$$C_1 = (Y_1 - C_{1+1} e^{h_{1+1} x_1} - C_{1+2} e^{h_{1+2} x_1} - \dots - C_n e^{h_n x_1}) e^{-h_1 x_1} \quad (4)$$

If the peak heights, Y_i , are constant, each C_i is constant and y is a function only of the channel number. Equation 3 can be expressed as a power series:

$$y = \sum_{i=1}^n C_i + x \sum_{i=1}^n C_i h_i + x^2 \sum_{i=1}^n \frac{C_i h_i^2}{2!} + \dots \quad (5)$$

In an ideal spectrum, the data could be fitted either by non-linear regression (Equation 3) or by linear regression (Equation 5). In practice, however, the counting rates in the ^{227}Ac spectral region are so low and the data so scattered that the tailing can be approximated equally well by a straight line.

Figure 6a shows part of the spectrum of a ^{227}Ac source 30 min after separation of ^{223}Ra by method A. The slope and intercept of the straight line were computed by least squares from the data between 4.1 and 4.7 MeV. The spectra in Figures 6b, 6c and 6d, respectively, are from the same source 9, 19 and 33 days later. The extrapolated lines appear to fit the scattered data reasonably well; there is no apparent correlation between the age of the source and the computed values of the intercept and slope. Attempts to use quadratic and higher-order polynomial versions of Equation 5 were generally less successful because of the inadequacy of the data.

In a real alpha spectrum the magnitude of a peak can be determined more precisely from the integrated area under the peak than from the peak height, since many observed peaks are composites of two or more real peaks whose energies are too close to be resolved. Even when the peak is mono-energetic and isolated from interference (e.g., the ^{215}Po peak at 7.384 MeV) it is usually asymmetrical and the highest observed count is not necessarily identical with the theoretical peak height.

We, therefore, define an area in Figure 5, bounded by channels a and b, which represents the combined tailing interference under the three small peaks located in channels z_1 , z_2 and z_3 . The integrated counting rate in this spectral region is:

$$\int_a^b y dx = A_1 (b - a) + A_2 (b^2 - a^2) + A_3 (b^3 - a^3) + \dots \quad (6)$$

where:

$$A_j = \sum_{i=1}^n \frac{C_i h_i^{j-1}}{j!} \quad (j = 1, 2, 3, \dots, \infty) \quad (7)$$

Since the counting rate of ^{227}Ac is constant for experiments of relatively short duration, it can be represented by a constant, A_0 . The observed counting rate between channels a and b will then be

$$A_c = A_0 + A_1 (b - a) + A_2 (b^2 - a^2) + A_3 (b^3 - a^3) + \dots \quad (8)$$

FIGURE 6 - Detail of ^{227}Ac spectrum prepared by method A. The straight lines were computed from data between 4.1 and 4.7 MeV.

If b is held constant and a is varied between a_0 and a , the resultant family of equations, linear in the constants, can be treated by the method of least squares:

$$Ac_i = A_0 + A_1 (b - a_i) + A_2 (b^2 - a_i^2) + A_3 (b^3 - a_i^3) + \dots \quad (9)$$

where Ac_i is the sum of the observed counts between channels a_i and b .

Equation 9 is valid for a single spectrum in which the peak heights do not change significantly during data acquisition. However, in a non-equilibrium source, the spectrum is continually changing and the peak heights in successive spectra are not constant, but are functions of time. In the special case of sources separated by method A, it is assumed that all changes in peak heights are due to the growth of ^{223}Ra and its decay products, from which it follows that the change in each peak height, ΔY_i , can be expressed by

$$\Delta Y_i = k_i P_0$$

and each Y_i in Equation 4 should be replaced by

$$Y'_i = Y_i + k_i P_0$$

Integration of each constant in Equation 9 with respect to P_0 would then yield a quadratic equation:

$$A_i = f(P_0, P_0^2) \quad (10)$$

The following computational procedure was adopted: The upper limit of the ^{227}Ac spectral region (corresponding to b in Equation 9) was defined as 5.10 MeV, 0.15 MeV higher than the highest reported alpha energy of ^{227}Ac .¹¹ This allows for spectral shift, loss of resolution, and "pulse pile-up," which results when two alpha particles strike the detector simultaneously. The lower limit (corresponding to A_i in Equation 9) was defined, successively, as 4.70, 4.69, 4.68, ..., 4.10 MeV (for a channel width of 0.010 MeV).

After background correction, if any, the counts in each spectrum were integrated for each defined energy region, yielding a series of sums, Ac_i . The number of channels to be integrated was defined only once -- from the first spectrum, which was least subject to scattering interference. In all subsequent spectra, the channel number corresponding to 4.70 MeV was determined and each area integration was performed on the same number of channels for all spectra.

The summations in each spectrum were fitted to a truncated form of Equation 9:

$$Ac_i = A_0 + A_1 (5.1 - E_i) + A_2 (5.1^2 - E_i^2) \quad (11)$$

where Ac_i is the integrated area under the ^{227}Ac peaks between the energy limits 5.10 MeV and E_i ($E_i = 4.70, 4.69, 4.68, \dots, 4.10$ MeV). The summations, Ac_i , were weighted equally in the least squares computations.

A_0 was found to increase slightly with increasing age of the source, evidently due to the growth of ^{223}Ra and its decay products. Correction for this effect was made by fitting the computed values of A_0 , weighted inversely as the squares of their probable errors, to

$$A_0 = Ac^* + P_1 Po + P_2 Po^2 \quad (12)$$

where Ac^* is the constant counting rate of ^{227}Ac and P_1 and P_2 are arbitrary constants. The branching ratio was then:

$$B = \frac{Ac^*}{D^*} \quad (13)$$

Analysis of Sources Prepared by Method B A different approach is required for the analysis of spectra from initially pure ^{227}Ac into which both ^{227}Th and ^{223}Ra are growing. Since the decay of ^{227}Ac is negligible for experiments of relatively short duration (the decay factor $e^{-\lambda_1 t} = 0.999$ after 11 days), its effective alpha-counting rate can be written:

$$Ac^* = k_1 N_0 \lambda_1 B \quad (14)$$

where k_1 is the counting efficiency for ^{227}Ac and the other symbols are defined as in Equations 1.

In the spectral region 5.1 - 6.2 MeV, the effective counting rate of ^{227}Th is

$$Th^* = k_2 N_0 \lambda_1 (1 - B) \left(\frac{\lambda_2}{\lambda_2 - \lambda_1} \right) (1 - e^{-\lambda_2 T}) \quad (15)$$

where k_2 is the counting efficiency in that region for ^{227}Th , λ_2 is its decay constant, and T is the time between data acquisition and the separation time (T_0).

However, absolute purity of the ^{227}Ac at T_0 cannot be assumed; it is more likely that traces of both ^{227}Th and ^{223}Ra are present, and it is certain that both of these nuclides will grow significantly during the lengthy counting intervals demanded by the low specific alpha activity of ^{227}Ac . Furthermore, when a multichannel analyzer is operated in the live time mode, a real time error is introduced by the dead time of the analyzer. These factors combine to make the precise value of T uncertain.

To correct for this uncertainty, a constant, Δt , is added, which simultaneously compensates for the timing error and for residual ^{227}Th in the source by imposing an artificial T_0 , somewhat earlier than the real T_0 .

Let

$$C_1 = k_2 N_0 \lambda_1 (1 - B) \left(\frac{\lambda_2}{\lambda_2 - \lambda_1} \right)$$

and

$$T = t + \Delta t$$

where t is the observed time from separation to the end of the counting interval. Then,

$$Th^* = C_1 (1 - e^{-\lambda_2 t} e^{-\lambda_2 \Delta t})$$

and, since $e^{-\lambda_2 \Delta t}$ is constant:

$$\begin{aligned} C_2 &= -C_1 e^{-\lambda_2 \Delta t} \\ Th^* &= C_1 + C_2 e^{-\lambda_2 t} \end{aligned} \quad (16)$$

Since ^{223}Ra is growing in the spectral region 5.1 - 5.9 MeV, the observed counting rate in the region 5.1 - 6.2 MeV will be (from Equations 2):

$$Th = C_1 + C_2 e^{-\lambda_2 t} + C_3 Po \quad (17)$$

Equation 17 is linear in the constants and can be solved directly by the method of least squares.

If it is assumed that, in the region below 5.1 MeV, the tailing of ^{227}Th is a constant fraction, A_2 , of Th^* and the tailing and scattering interference from ^{223}Ra is a constant fraction, A_3 , of Po , the observed counting rate in that spectral region will be:

$$Ac = Ac^* + A_2 (C_1 - C_2 e^{-\lambda_2 t}) + A_3 Po \quad (18)$$

Since C_1 is the effective counting rate of ^{227}Th at equilibrium and $A_2 C_1$ is the counting rate of its tail,

$$B = \frac{Ac^*}{Ac^* + A_2 C_1 + C_1} \quad (19)$$

Results and Discussion

The branching ratios obtained from 12 sources, seven prepared by method A and five by method B, are presented in Table 2. The intermediate weighted means were $(1.3802 \pm 0.0069)\%$ and $(1.3799 \pm 0.0045)\%$, respectively. The grand mean for all 12 results weighted inversely as the squares of their internal probable errors was $(1.3800 \pm 0.0036)\%$. The results are consistent by Birge's criterion.¹⁶

Table 2

ALPHA-BRANCHING RATIO OF ^{227}Ac

Source Number	Method	Time Span (hr)		Number of Spectra	^{227}Ac (counts/hr)	Branching Ratio (%)
		Δt	t			
383767	A	-	595	284	677.7 ± 10.4	1.3735 ± 0.0211
383771	A	-	349	185	683.9 ± 19.0	1.5382 ± 0.0428
383795	A	-	254	135	1443.0 ± 49.2	1.3924 ± 0.0475
401321	A	-	253	125	2105.5 ± 36.6	1.4371 ± 0.0250
401325	A	-	800	373	886.6 ± 13.5	1.3751 ± 0.0210
386487	A	-	175	41	5411.7 ± 48.7	1.3755 ± 0.0124
386489	A	-	118	77	6267.8 ± 34.0	1.3734 ± 0.0074
Weighted Mean (A)						1.3802 ± 0.0069
386491	B	2.0	64	62	3314.5 ± 12.1	1.3583 ± 0.0140
386495	B	5.5	93	83	5652.9 ± 22.1	1.3847 ± 0.0088
386496	B	6.7	96	90	3187.3 ± 15.9	1.3669 ± 0.0117
386497 ^a	B	3.0	18	18	3320.2 ± 48.7	1.3581 ± 0.0566
386498	B	2.6	213	128	2605.9 ± 9.9	1.3864 ± 0.0066
Weighted Mean (B)						1.3799 ± 0.0045
Weighted Grand Mean						1.3800 ± 0.0036

^aExperiment prematurely terminated by instrument failure.

As pointed out earlier, the value of $(1.45 \pm 0.06)\%$ reported by Nurmi et al.,⁴ was based on an erroneous half-life value for ^{227}Th and on some approximations which were not used in this work (e.g., the assumption that the counting rate of ^{223}Ra is identically equal to that observed for ^{215}Po . Cf. Table 3). Nevertheless, that result and the one reported here agree within one probable error.

Table 3
 ^{223}Ra CORRECTION FACTORS FOR VARIOUS SOURCES

Source Number	Method ^a	r (5.11 - 6.20 MeV)	q (4.10 - 6.20 MeV)
383767	A	1.1691 ± 0.0010	1.2077 ± 0.0010
383771	A	1.2107 ± 0.0017	1.2796 ± 0.0018
383795	A	1.2410 ± 0.0017	1.3215 ± 0.0018
401321	A	1.1054 ± 0.0014	1.1447 ± 0.0014
401325	A	1.1075 ± 0.0009	1.1471 ± 0.0009
386487	A	1.2011 ± 0.0015	1.2855 ± 0.0016
386489	A	1.1178 ± 0.0017	1.1516 ± 0.0017
386491	B	0.9150 ± 0.0835	0.8633 ± 0.0873
386495	B	1.2864 ± 0.0367	1.2944 ± 0.0388
386496	B	1.3482 ± 0.0488	1.3239 ± 0.0504
386497	B	1.2561 ± 0.7232	1.5027 ± 0.7409
386498	B	1.2435 ± 0.0107	1.2874 ± 0.0111

^a Sources prepared by method A were ignited; sources prepared by method B were heated to 200°C but not ignited.

No consideration has been given to tailing by alpha particles from ^{227}Ac , and the randomness of the data from sources prepared by method A precludes such a determination. However, for sources prepared by method B, in which ^{227}Th and ^{223}Ra interference was slight, it was found that ^{227}Ac tailing was indeed negligible. It may therefore be assumed that the same would be true for method A. The credibility of the reported branching ratio is enhanced by the fact that two totally independent methods gave nearly

identical results. Nevertheless, the significance of method A lies less with the branching ratio than with the computational techniques developed for its determination.

The data in Table 1 illustrate the constancy of Th^* and D^* , as computed by Equations 2 for a typical source prepared by method A. It is noteworthy that r and q , the ratios of ^{223}Ra to ^{215}Po in the two designated spectral regions, are both constant and significantly different from unity. However, these values, indicative of the loss of ^{219}Rn from the source by alpha recoil, are not identical for all sources (Table 3), but must be individually determined.

The technique of correcting the apparent ^{227}Ac counting rate for tailing by ^{227}Th and ^{223}Ra should prove useful as an analytical tool, provided that the resolution of the spectrum is sufficiently good and the counting rate of ^{227}Ac is sufficiently high with respect to the interferences. For nuclides with higher specific activity and better counting statistics than those possible with ^{227}Ac , the polynomial form of Equation 8 could be used without truncation.

For sources of ^{227}Ac in which both ^{227}Th and ^{223}Ra are growing (or decaying) significantly, the imposition of an artificial T_0 should prove useful as an analytical technique. The computed value of Δt (Table 2) ranged from 2.0 to 6.7 hr; since the time t was taken as the end of the counting interval, this implies that from 0.16 to 0.89% of the original ^{227}Th remained in the source after separation. There was no apparent correlation between the amount of residual ^{227}Th and the computed branching ratio. (H. W. Kirby)

Inorganic Chemistry

STABILITY OF HYDRIDIC RARE EARTH COMPOUNDS

In recent times, new rare earth compounds have been prepared and characterized.¹⁷ These compounds have been found to be oxide hydrides with the fluorite-type structure, and may be prepared by dissolving elemental lanthanides in acids such as acetic acid, substituted acetic acids, propionic acid and propiolic acid. Recent experimentation with gadolinium metal suggests that the gadolinium member of this new series of rare earth compounds may also be prepared by dissolving gadolinium metal in warm, aqueous sodium hypochlorite. By whatever method of preparation, however, some anions of the acid used in the preparation of these compounds always remain in the compounds.

One of the curious aspects of these compounds is the apparent selectivity of the lanthanide elements toward various acids in the preparative reaction. Thus, while the acids cited above may be used to prepare the hydridic compounds, other acids such as hydrobromic cannot be used. This suggests that the bromide ion is so much larger than the oxide ion or coordinated oxide ion (as in acetic acid) that the resulting fluorite structure is unstable. The failure of butyric acid to yield the new hydridic lanthanide compounds suggests that the butyrate ion is so large that it cannot be accommodated in the fluorite lattice. Mucochloric acid may form the compounds because the oxygen atoms at the ends of the molecule can perhaps span two lattice sites, suggesting the possible formation of a semiconductor. Formic acid apparently does not produce these new compounds. In the case of formate, the hydrogen atom remaining in the formate radical may be slightly acidic, or may at least be delegated somewhat more of an incremental positive charge than is ordinarily found on aliphatic hydrogen atoms. This incrementally positive hydrogen atom cannot exist for long periods in the neighborhood of hydride ions without reacting to form hydrogen gas. This internal reaction between the hydride ions and the remaining proton on the formate radical prevents the formation of the hydridic lanthanide preparations with formic acid. Similarly with methyllactic acid, the proton bound to the hydroxyl group on this acid radical perhaps cannot exist for long periods near hydride ions without a destructive internal reaction leading to hydrogen gas. In the case of sulfate, the bisulfate radical is known to be a weak acid. A proton coordinated to one of the oxygen atoms in the sulfate radical in the fluorite lattice would also find itself in the neighborhood of hydride

anions. The disruptive internal reaction which would follow may explain the sensitivity of the hydridic rare earth compounds to sulfate. Thus, the sensitivity of the fluorite hydrides to sulfate and the sensitivity of plutonium oxide, another fluorite-type oxide, to sulfate¹⁸ may not be as unrelated as would first appear. An analogous reaction does not occur with perchlorate because of the inability of protons to associate strongly with the oxygen atoms in the perchlorate radical. (G. L. Silver)

Separation Chemistry

URANIUM-234 RECOVERY

During the anion exchange recovery process used at Mound for the recovery and purification of plutonium-238, uranium tends to be washed off the column, winding up in the waste raffinate solution. Because of the large quantities of aged plutonium-238 processed in the recovery system, this raffinate solution represents a rich source of uranium-234. Previous laboratory-scale work¹⁹ had shown that extraction with tri-n-octyl phosphine oxide (TOPO) would give efficient recovery and good concentration factors with a minimum of equipment and a simple process. Therefore, a uranium-234 solvent extraction recovery facility was designed and constructed and now is in operation.

The uranium-234 recovery facility consists of three separate alpha-tight boxes or box lines which have been designated "transfer," "solvent extraction," and "processing." The transfer box contains two 200-liter tanks, 24 in. (60 cm) in diameter and 30 in. (76 cm) high. Double-walled polyethylene transfer lines connect these tanks with the plutonium-238 anion exchange processing areas, and solutions are transferred into these tanks by vacuum. The transfer tanks are fitted with sight gages, which have been calibrated and provide a convenient method of determining solution volumes. The transfer box is hung from the ceiling so that the bottoms of the tanks are approximately 7 ft (2.1 m) above floor level. Two stainless steel transfer lines service the solvent extraction box: one for gravity transfer of the raffinate solution to the mixing tanks, and the second for vacuum transfer of waste solutions back to the transfer tanks. Another line connects the transfer tanks to the waste disposal facilities, and transfers can be made by either gravity drain or by vacuum.

The solvent extraction box is 10 ft (3.05 m) long, 7 ft (2.1 m) high, and 3 ft (0.9 m) deep, and contains three mixing tanks and a number of storage tanks. Two of the mixing tanks have a capacity of 70 liters each and are 20 in. (50.8 cm) in diameter and approximately 18 in. (45 cm) high. The bottoms of the tanks are cone shaped and fitted with Pyrex glass pipe reducers [4 in. (10.1 cm) to 1 in. (2.5 cm)] to permit visual observation of the interface while making a separation of the organic and aqueous phases. The mixing tanks are also fitted with sight glasses (opposed 180°) and a fluorescent light, to give some visual indication of what is happening inside the tanks. The smaller, 12-liter capacity, mix tank is

of similar construction, with a diameter of 8 in. (20.3 cm) and a height of approximately 13 in. (33 cm). This tank is also fitted with a Pyrex glass pipe reducer [4 in. (10.1 cm) to 1 in. (2.5 cm)], and with sight glasses and a light. All three mix tanks are fitted with 1/4-hp variable-speed stirring motors. Two 3-in. (7.6-cm) diameter impellers are used for each tank: one just above the glass pipe adaptor section, and a second one near the top of the tank. Baffles were installed in the tanks to prevent vortexing.

In addition to being serviced by the two transfer tanks, four reagent tanks (25 to 50-liter capacity) are located above and outside the box. The reagent tanks are filled by vacuum transfer and drain into the box by gravity. Two reagent tanks are used for concentrated HNO_3 and 2M HNO_3 , which are house services, while the other two are used for other required liquid reagents.

In the bottom of the solvent extraction box are six polyethylene holding tanks. Two of approximately 130 liters capacity are used to collect the aqueous solution after it has been extracted, and hold it until it is convenient to transfer to waste disposal. Two tanks of 50 liters capacity and two tanks of 30 liters capacity are used to hold various intermediate process solutions. Solutions are transferred into the holding tanks by gravity, but must be emptied by vacuum. A 10-liter transfer tank, located near the top of the box, permits vacuum transfers within the box and is also used to transfer solutions to and from the processing box. In addition, the mixing tanks are vacuum tight, and can be used to transfer solution from the holding tanks to the mixing tanks for further processing.

The processing box line consists of two standard 3-ft (0.9-m) alpha boxes. The only special equipment is a 10-liter transfer tank and the piping necessary to vacuum transfer to and from the transfer tank in the solvent extraction box. The remaining equipment in the processing line is standard laboratory type equipment such as hot plates, stirrers, beakers, bottles and filtration equipment.

The extracting agent is 0.1M TOPO* dissolved in Amsco "Odorless Insecticide Base."[†] The anion exchange raffinate solution is 7.2M in HNO_3 and typically contains 1-3 mg/liter of uranium and a similar amount of plutonium. A wide variety of metal ion impurities may be present, and some may be present in gross amounts (especially iron). Anion impurities include fluoride and sulfate. Previous work¹⁹ had indicated no interference from the expected impurities in modest amounts, and that single-stage extractions would recover 99% of both the plutonium and the uranium.

*(C_8H_{17})₃P=O, F.W. = 386; m.p. = 55-57°C; from Carlisle Chemical Works, Inc., Reading, Ohio.

[†]A purified kerosine fraction; specific gravity 0.764; distillation range 183-271°C; flash point 135°F; from Amsco Solvents and Chemicals Co., Cincinnati, Ohio.

Even repeated extractions of synthetic solutions with the same organic gave 90% recoveries with concentration factors of several hundred. The details of the plutonium-238 recovery process have changed slightly from the method proposed during the development work, but are basically the same. The current procedure is as follows:

1. With 15-20 liters of organic extractant in the mix tank, transfer in 40-50 liters of feed solution and 1 liter of 1.6M $\text{Al}(\text{NO}_3)_3$ to complex fluoride ion. Stir for 15-30 min and allow the phases to separate. Drain the aqueous phase to a holding tank.
2. Repeat the extractions in the same mix tank until all of the feed solution has been processed, or until the organic phase is loaded.
3. Strip the organic phase by repeated contacts (stirring for 5 min at reduced speed) with 2-liter batches of 1.0M Na_2CO_3 or other suitable stripping agent. After the phases separate, carefully remove the aqueous phase and transfer it to the processing box.
4. Slowly add the strip solution, with stirring, to a sufficient amount of concentrated HNO_3 to make the final solution about 1M in acid. Heat to expel carbon dioxide.
5. Neutralize and precipitate by adding NaOH . Digest the precipitate for several hours on a hot plate. After allowing the precipitate to cool and settle overnight, decant off the bulk of the supernatant solution and filter the remaining slurry.
6. Transfer the precipitate to a beaker, slowly add concentrated HNO_3 and heat for several hours. Dilute with 0.35M HNO_3 and filter the solution. Wash and discard the residue.
7. Analyze the product solution from step 6 for plutonium, uranium, and acid.

An optional plutonium separation step consists of adjusting the resulting solution to 2M HNO_3 and precipitating plutonium oxalate homogeneously.^{20,21} After the plutonium oxalate is removed by filtering, the solution is ready for further processing and purification.

At this point, the product solution leaves the recovery facility and is taken to a regular processing alpha hood line. The solution at this point typically contains 0.2-2.0 g of uranium, 0.05-0.50 g of plutonium, 1-3M HNO_3 , and has a volume of 200-500 ml. Several small batches, of similar composition, may be combined at this point. Additional processing may vary according to the characteristics of the product, but generally is directed toward the removal of plutonium. Typical processing consists of the following steps:

1. Salt the product solution from step 6 or from the additional plutonium removal step with $\text{Al}(\text{NO}_3)_3$ to a concentration of 1.6M and load on an anion exchange column (Dowex 1X4). Wash with 9M HCl, then with 9M HCl/0.04M I^- to remove plutonium. Elute the uranium with 0.1M HCl.
2. If the first cycle of anion exchange does not remove all of the plutonium, evaporate the eluate to dryness, take up in dilute HNO_3 , salt with $\text{Al}(\text{NO}_3)_3$ and repeat the anion exchange step until the desired purification is achieved.
3. Evaporate the uranium product solution to dryness, take up in dilute HNO_3 and precipitate the uranium with NH_4OH . Filter, collecting the precipitate on "ashless" filter paper. Dry the precipitate and calcine to constant weight at 800°C.

Summary of Operations

Batch U-1: Extraction of solutions stored in drums. Processing of the strip solution gave no precipitate, and all solutions were recycled.

Batch U-2: Addition of aluminum nitrate solved the extraction problems. Extraction of raffinate from the processing of more than 100 g of plutonium. Recovery of 0.042 g of plutonium-238 and 0.2 g of uranium-234 at 98% isotopic purity.

Batch U-3: Extraction of 340 liters of low-level raffinate from current plutonium-238 recovery operations. Recovery of 0.3 g of plutonium-238 and nearly 2 g of uranium-234 at 94% isotopic purity.

Batch U-4: Re-extraction of 175 liters of raffinate which had been stored in drums (two stages of extraction). Recovery of an estimated 0.7 g of plutonium-238, but homogeneous oxalate precipitation removed all but 0.22 g which accompanied the 0.8 g of uranium-234. Isotopic purity was about 95%.

Batch U-5: Extraction of 600 liters of low-level raffinate from current plutonium-238 recovery operations. Product has been stripped and concentrated but not analyzed.

During the processing to date, several problems have arisen, and some of these are only partially solved. One of the basic problems is that of analysis of various intermediate process solutions. In the original concept, the process was felt to be insensitive to the expected variations, and little or no process control would be necessary. In the processing of the first batch, it became apparent that additional information was needed. The movement of the plutonium is the easiest to follow, and requires only the sampling and mounting of planchets for alpha counting. For aqueous solutions this service is rapidly and adequately performed; for organic solutions the techniques are still being developed, so that

meaningful data are available, but more effort is required. Thus, plutonium analyses are generally available one day after the samples are taken. Uranium analyses, however, typically require several weeks before the results are available. Therefore the tendency has been to analyze for plutonium only, and to extrapolate to the behavior of the uranium.

The problem observed in the first batch was non-extraction of the plutonium. Generally, the feed solutions are not analyzed prior to extraction, but the general plutonium concentration is known from previous processing. In this case, alpha counts for the extracted solutions were quite varied but on the same order of magnitude as for the feed solution. Also, precipitation of the strip solution produced only a very small amount of precipitate, which looked and behaved like iron. After a number of laboratory-scale extraction tests it was found that the addition of $\text{Al}(\text{NO}_3)_3$ solution greatly enhanced the extraction of plutonium (and presumably of the uranium) and that addition of 2 vol % of 1.6M $\text{Al}(\text{NO}_3)_3$ would produce acceptable extractions, with minimum addition of aluminum. The cause of the non-extraction is believed to be an iron(III)-fluoride complex, which can be present in such large amounts as to prevent extraction of the plutonium and uranium, and which is sufficiently stable that it is not stripped well by sodium carbonate. In any case, the addition of the aluminum seems to have solved the problem of non-extraction. The evidence also supports the belief that the extent of uranium extraction parallels the extent of plutonium extraction, and can be monitored by alpha counting the extracted solutions.

Stripping of the loaded organic continues to be a problem. One contributing factor is that only a single cycle of extraction and stripping is being used, rather than the initially proposed method of two cycles, and small volumes of stripping agents are used in an effort to obtain maximum concentrations. Typically, the loaded organics from both large mix tanks are combined (30 to 35 liters) and contacted with 2 to 3-liter portions of stripping agents. Process runs for which analytical data are available are summarized in Table 4. In batch U-3, counting of the organic indicated little or no plutonium had been stripped, and this was confirmed when the strip solution was analyzed, but there apparently was good stripping of the uranium. In this case (and apparently in the general case), during stripping, the behaviors of uranium and plutonium are not parallel, and here the uranium is stripped more easily. Complete stripping of the plutonium is desirable to avoid loss of capacity of the organic phase and, therefore, various stripping agents were used in successive batches. The most successful to date was the stripping of batch U-4 where the organic was contacted with oxalic acid as a complexing agent, followed by hydroxylamine as a reducing agent plus fluoride as a complexing agent, then stripped with sodium carbonate solution. Interestingly, while they did not remove much plutonium, the first two solutions stripped out a large amount of hydroxide-insoluble material (which looked like iron), but it is still unknown where the uranium comes out due to the analytical problem.

Table 4

PROCESS-SCALE STRIPPING

	Plutonium	
	(mg/liter)	Total (g) ^a
<u>Batch U-3</u>		
Loaded Organic	28	0.98
After Contact with 3 liters of 0.66M Na ₂ CO ₃ / 0.03M (NH ₄) ₂ C ₂ O ₄	27	0.94
Repeat of Above	39 ^b	- -
Combined Strip Solution		0.30
<u>Batch U-4</u>		
Loaded Organic	21	0.735
After Contact with 2 liters of 0.25M H ₂ C ₂ O ₄	20	0.70
After Contact with 2 liters of 0.35M NH ₂ OH-HNO ₃ / 0.4M HF	19	0.665
After Contact with 2 liters of 0.5M Na ₂ CO ₃	0.42	0.015
Repeat of Above	n.a. ^c	- -
Combined Strip Solution		est 0.7
<u>Batch U-5</u>		
Loaded Organic	not sampled	
After Contact with 2 liters of 0.25M H ₂ C ₂ O ₄	14.3	0.50
After Contact with 2 liters of 1.0M Na ₂ CO ₃	12.4	0.43
Repeat of Above	5.4	0.19
Combined Strip Solution		n.a. ^c

^a Assuming an organic volume of 35 liters.^b Solids suspended in organic.^c Not yet analyzed.

Concurrent with the processing, a number of laboratory-scale tests were run to gain more insight into possible stripping methods. A partially loaded organic solution from the process, analyzed to contain 11.5 mg/liter of plutonium-238, was used in all of these experiments. Each test consisted of contacting 3 ml of the stock organic with 1 ml of a test stripping agent. After separation each phase was alpha counted, and stripping efficiency and losses were calculated. The stripping solutions and results are listed in Table 5. In the first four tests, the effects of $\text{H}_2\text{C}_2\text{O}_4$ and Na_2CO_3 in various combinations were examined. Interestingly, $\text{H}_2\text{C}_2\text{O}_4$ alone stripped 16%, carbonate alone stripped 26% and, when the solutions are combined, the effect seems to be additive. However, when the $\text{H}_2\text{C}_2\text{O}_4$ was added to the organic first and shaken, then the carbonate added and shaken, the stripping efficiency was increased by 30%. This effect was also observed in the case of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and Na_2CO_3 (tests 5 and 6), where sequential addition of reagent resulted in nearly twice the stripping efficiency compared to stripping with the mixture. No explanation of this behavior will be attempted, except to suggest that some of these reactions may be quite pH-dependent. Two tests with peroxide (tests 8 and 9) indicate that the peroxide has little effect on the stripping of plutonium. The tests with HF and KF show that at high concentrations fluoride is an efficient stripping agent, but at these concentrations corrosion of equipment would be a problem. At lower concentrations (e.g., 0.1M) fluoride is rather poor. The last test is a procedure which has been used with great success in an analytical determination²² to prevent the extraction of plutonium from aqueous solution into TOPO. Normally this treatment would remove more than 99% of the plutonium, and shows how tightly at least part of the plutonium is being held.

In order to observe both the uranium and plutonium during the stripping, a sample of plutonium-238-loaded organic was spiked with sufficient uranium-233 so that the uranium-233 and plutonium-238 alpha activities were approximately equal. Count and analysis indicated that the resulting solution contained 7.9 mg/ml of uranium-233 and 4.6 $\mu\text{g}/\text{ml}$ of plutonium-238. A 3-ml portion of organic was shaken with a series of 1-ml portions of stripping agents, and the solutions were analyzed after separation. In the first stripping sequence an attempt was made to approximate the conditions used to strip batch U-4 (see Table 4). The procedure was:

1. Contact with 0.5M oxalic acid--A copious yellow precipitate appeared in the organic, either sticking to the wall of the separatory funnel or riding on the top (organic side) of the interface. The strip solution contained 37% of the plutonium, no uranium.
2. Contact with 0.35M $\text{NH}_2\text{OH}-\text{HNO}_3$ --No apparent effect on the precipitate from above. Strip solution contained an additional 30% of the plutonium, no uranium.
3. Contact with 0.5M Na_2CO_3 --Strip solution contained 14.5% of the uranium, an additional 20% of the plutonium.

Table 5

LABORATORY-SCALE STRIPPING EXPERIMENTS

<u>Test No.</u>	<u>Procedure</u>	<u>Stripping Efficiency (%)</u>
1.	0.1 ml of 0.5M $\text{H}_2\text{C}_2\text{O}_4$ was added to the organic, shaken, 1.0 ml of 0.5M Na_2CO_3 was added, shaken, and phases were separated.	55
2.	Same as 1, but acid and carbonate were premixed before use.	42
3.	1.0 ml of 0.5M Na_2CO_3 was used.	26
4.	1.0 ml of 0.045M $\text{H}_2\text{C}_2\text{O}_4$.	16
5.	0.1 ml of 0.5M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ was added to the organic, shaken, 1.0 ml of 0.5M carbonate was added, and shaken.	50
6.	Same as 5, but oxalate and carbonate were premixed.	26
7.	1 ml of 0.05M HNO_3 premixed with 2 drops of 48% HF (estimated 2.5M HF).	97.5
8.	1 ml of 0.05M HNO_3 premixed with 0.1 ml of 30% H_2O_2 .	0
9.	1 ml of 0.5M carbonate premixed with 0.1 ml of 30% H_2O_2 (much gassing, and precipitate stuck to glass).	29
10.	1 ml of 0.1M HF.	12
11.	1 ml of 0.1M KF.	15
12.	1 ml of 0.5M KF.	77
13.	1 ml of 1.0M KF (some plutonium precipitated on glass).	70
14.	1 ml of 0.5M HF [some additional plutonium dissolved from the walls (see step 13)].	57
15.	1 ml of 0.25M H_2SO_4 .	10
16.	2 ml of 2N HNO_3 to which had been added, in sequence, with stirring, NaF, $\text{NH}_2\text{SO}_3\text{H}$ and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (see reference 22).	63

4. Contact with 0.5M Na_2CO_3 --Strip solution contained 32% of the uranium and 17% of the plutonium.

5. Since some uranium remained on the walls of the separatory funnel, the organic was contacted with a 1M HNO_3 rinse.
This put most of the uranium back into the organic phase.

The results are summarized in the top half of Table 6. In comparing these results with the stripping behavior of batch U-4, it must be remembered that the uranium concentration was perhaps a thousand times higher in the uranium-233-spiked solution than in the process solution, which explains the precipitation encountered in the spiked solution.

Table 6

STRIPPING OF URANIUM-233-SPIKED ORGANIC SOLUTION

Stripping Agent	Uranium Stripped (%)		Plutonium Stripped (%)	
	Actual	Cumulative	Actual	Cumulative
0.5M $\text{H}_2\text{C}_2\text{O}_4$	0	0	37	37
0.35M $\text{NH}_2\text{OH}-\text{HNO}_3$	0	0	30	67
0.5M Na_2CO_3	14.5	14.5	20	87
0.5M Na_2CO_3	32	48.5	7	94
1M HNO_3	0	48.5	0	94
(Left in organic)	(33)	81.5	(9)	103
0.5M Na_2CO_3	73	73	39	39
0.5M Na_2CO_3	14.5	87.5	21	60
0.5M Na_2CO_3	7	94.5	14	74
0.5M Na_2CO_3	2.8	97.3	4.8	78.8
0.5M Na_2CO_3	1.5	98.8	4.3	83.1
(Left in organic)	(1.8)	100.6	(8.4)	91.5

In the second stripping sequence, five 1-ml portions of 0.5M Na_2CO_3 were used to strip the organic, with the results listed in the lower half of Table 6. The stripping behavior here seems to correspond to that found in the stripping of batch U-3 where the uranium, but very little plutonium, was removed.

The uranium-234 products from batches U-2, U-3 and U-4 were each given one cycle of anion exchange purification, then combined and given two additional cycles of anion exchange purification. After conversion to U_3O_8 the weight of the product was 4.10 g. A shipment of 4.07 g (3.44 g of uranium; 3.23 g of uranium-234) was made to the Heavy Elements Research Pool at ORNL. This material was designated A-11 8/69 and contained 28 ppm (by weight) of uranium-232 and 5.1 ppm (by weight) of plutonium-238. Isotopic purity was 93.76% with 6.08% mass, 238, 0.09% mass, 235, 0.05% mass, 236, and 0.02% mass, 233. Emission spectrographic analysis indicated the presence of small amounts of iron, chromium, calcium, nickel, zinc and magnesium. (P. E. Figgins and M. R. Hertz)

THORIUM-229 RECOVERY

All planned analyses on the 42 26-gal (98.4-liter) drums of Nuclear Fuel Services uranium-233 purification raffinate have been completed. Spectrophotometric thorium analyses were run on samples from the six drums for which thorium concentrations below the measurable limits for instrumental analysis were reported. A summary of the completed analytical work is given in Table 7.

The unexpectedly high total thorium content of the raffinate, totalling more than 150 kg for the 42 drums, indicates the use of large amounts of natural thorium as a salting agent by NFS. It also eliminates the use of the planned simplified solvent extraction method for concentrating thorium-229 from the raffinate because of saturation of the organic with thorium. Because of the high ratios of total thorium to thorium-229 (varying from drum to drum from 90 to 8,000,000) in any product which might be obtained, plans for future processing of the raffinate are uncertain. Processing of drum No. 32, which contains 10 mg of thorium-229 associated with only 90 times its weight in natural thorium, is being considered.

In view of the results obtained with the NFS material, processing of the uranium-233 "cow" on hand was resumed. One run, in which 1.6 mg of thorium-229 were recovered from 11-yr-old UF_4 containing 39 g of uranium-233, was completed and the product was shipped to the Heavy Elements Research Pool at ORNL. A rough weight assay was made on the product, indicating that impurities, including other thorium isotopes, did not constitute more than seven times the thorium-229 weight. (M. R. Hertz and R. M. Watrous)

Table 7

NFS RAFFINATE—SUMMARY OF ANALYTICAL WORK

Drum No.	Thorium (mg/drum)	Thorium % Extracted Single Stage	Calcined Solids		Amount Deposited from Organic ^a	Total Thorium (mg/ml) ^b	Th/ ²³² Th Ratio
			(g/l)	(kg/drum)			
1	4.1	100	12	1.2	+	0.074	1,800
2	4.2	100	24	2.4	+	0.216	5,100
3	3.5	100	24	2.4	++	0.011	310
4	2.7	100	24	2.4	++	0.018	660
5	2.6	19	42	4.1	++++	17	6.4×10^5
6	3.0	7	72	3.0	++	56	18×10^5
7	0.7	14	94	9.3	+	45	63×10^5
8	1.3	31	42	4.1	+	17	13×10^5
9	1.2	100	30	3.0	++	0.053	4,300
10	8.2	0	22	2.2	++	>75	$>9 \times 10^5$
11	6.8	0	196	19	+++	>75	$>11 \times 10^5$
12	2.8	0	66	6.5	+++	10	35,000
13	22.8	16	68	6.7	+++	22	95,000
14	24.1	10	40	3.9	+++	24	98,000
15	26.2	4	46	4.5	+++	28	1.1×10^5
16	22.0	17	56	5.5	+++	19	85,000
17	14.5	2	48	4.7	+++	18	1.2×10^5
18	1.0	70	24	2.4	+++	6	5.9×10^5
19	1.0	40	192	18.9	++	10	9.8×10^5
20	37.3	5	182	17.9	++++	>75	$>2 \times 10^5$
21	22.7	7	182	17.9	++++	>75	$>3.2 \times 10^5$
22	8.6	0	134	13.2	++++	>75	$>8.6 \times 10^5$
23	10.8	8	124	12.2	++++	>75	$>6.8 \times 10^5$
24	1.1	9	206	20	+++	8	$>7.2 \times 10^5$
25	1.1	9	92	9.1	++	45	40×10^5
26	13.1	21	50	4.9	+++	7	53,000
27	15.5	23	42	4.1	+++	20	1.3×10^5
28	14.4	11	66	6.5	+++	>75	$>5.1 \times 10^5$
29	5.7	23	108	11	++	>75	$>13 \times 10^5$
30	9.5	14	56	5.5	+++	29	3.0×10^5
31	13.0	68	46	4.5	++++	9	68,000
32	9.9	100	12	12	++	0.009	89
33	1.0	0	56	5.5	++	31	31×10^5
34	0.7	0	82	8.1	+++	50	70×10^5
35	0.6	0	70	6.9	+++	37	60×10^5
36	0.6	0	74	7.3	+++	45	70×10^5
37	0.6	0	90	8.9	+	50	80×10^5
38	0.7	0	90	8.9	+	60	80×10^5
39	2.7	11	54	5.3	+++	>75	$>28 \times 10^5$
40	2.7	11	30	3.0	++	>75	$>28 \times 10^5$
41	3.9	0	26	2.6	++	13	3.3×10^5
42	9.3	100	4	0.4	++	6	63,000

^aRelative amounts of solids calcined on counting planchet from 0.050 ml TOPO-DEB organic from first extraction determined by visual inspection.

^bEmission spectroscopy results except for those less than 3 mg/ml which are by spectrophotometry.

Analytical Chemistry

ANALYSIS OF THE SIXTH COOPERATIVE BORON SAMPLES AND HIGH PURITY BORON

Mound Laboratory participated in the recent analysis of the Sixth Cooperative Boron Samples and High Purity Boron. The total boron and the impurities in these samples have been determined by various techniques and the results of analysis are compared in Table 8. Good agreement was obtained for impurity determinations between emission spectroscopy and atomic absorption spectrophotometric results.

A Perkin-Elmer atomic absorption spectrometer Model 303 equipped with a Model DCR-1 digital concentration readout was used to determine the impurities. The procedures used for the impurity analyses are those given in the manual.²³ The boron solution used for the analysis was prepared by refluxing a 0.1 to 0.5-g sample of boron (sample size depending on the impurity level) with 15 ml of concentrated HNO_3 for 16 to 20 hr. The acid sample was then diluted to 50 ml, cooled, and filtered into a 100-ml volumetric flask. The filter paper was washed several times with distilled water, and then final dilution to the mark was made.

Composite standard solutions were prepared by adding the appropriate quantities of standard metals in solution to 100-ml volumetric flasks containing 15 ml of concentrated HNO_3 and diluting these to the mark. If further dilutions were necessary, 15 vol % HNO_3 was used as the diluent.

Chromium, copper, iron, magnesium, nickel and manganese were determined with an air-acetylene flame. Calcium was determined with a nitrous oxide-acetylene flame. The concentration of the desired metal in the sample solution was obtained either from a calibration curve or directly from the concentration readout. The accuracy for the method is approximately $\pm 5\%$, except for extremely low concentrations.

A Jarrell-Ash 3.4-m Ebert spectrograph and source was used to determine impurities by emission spectroscopy. Three samples of boron (6, 3 and 1 mg) were each mixed with approximately 24 mg of 1:4 barium carbonate buffer in an SPK-4261 electrode (the samples were firmly packed and vented to prevent sample loss during carbonate decomposition). The electrodes with the samples were "burned" at 17 A. The sample plate was compared

Table 8

ANALYTICAL DATA FOR THE BORON SAMPLES

Desired Constituent	Sample F 4359 (wt %)			Sample F 4360 (wt %)			Sample F 4078 (wt %)	
	Emission Spectroscopy	Atomic Absorption	Other Method	Emission Spectroscopy	Atomic Absorption	Other Method	Emission Spectroscopy	Other Method
B			93.8 ^a			93.8 ^a		99.5 ^a
H ₂ O			0.16 ^b			0.13 ^b		0.06 ^b
C			0.99 ^c			0.75 ^c		0.29 ^c
O			0.11 ^d			0.92 ^d		0.019 ^d
H			0.31 ^d			0.59 ^d		0.017 ^d
N			0.009 ^d			0.004 ^d		0.035 ^d
Si	0.13	- -		0.12	- -		0.024	
Fe	0.3	0.43		0.14	0.19		- -	
Mn	0.09	0.06		0.05	0.03		- -	
Mg	0.014	0.009		0.04	0.03		<0.001	
Cr	0.6	0.48		0.25	0.2		0.009	
Ni	1.8	2.1		1.8	1.6		0.013	
Al	<0.001	- -		<0.001	- -		<0.001	
Ca	0.1	0.05		0.3	0.24		0.02	
Cu	1.8	1.5		1.8	1.1		0.002	
Ag	<0.001	- -		<0.001	- -		<0.001	
Ti	0.03	- -		0.01	- -		- -	

^aBoric acid titration in presence of mannitol.

^bLoss in weight - drying in oven at 110°C.

^cLeco carbon analyzer.

^dVacuum fusion.

visually with a calibrated standard plate of Spex Mix prepared in the same manner as the samples. The accuracy by this method is $\pm 50\%$.

The oxygen, nitrogen and hydrogen values were obtained with a National Research Corporation vacuum fusion analyzer. The general procedures are from the manual²⁴ accompanying the instrument, in which a 20 to 30-mg sample of boron encapsulated in platinum was dropped into a degassed molten platinum bath at 2100°C. The volume of evolved gas was pumped to the measuring system and circulated through the analytical system in the manner prescribed in the manual for the determination of oxygen, nitrogen and hydrogen.

Moisture was determined by oven drying 3 to 5-g samples of boron for 2 hr at 110°C. Carbon was determined by the combustion method using the Leco gasometric carbon analyzer and the procedure supplied with the analyzer. (L. L. Bentz, J. O. Frye and Y. G. Ishida)

INFRARED ANALYSIS OF WATER IN 2-ETHYL-1-HEXANOL

An investigation was conducted to determine if a spectrophotometric technique could be used in-line to analyze water in 2-ethyl-1-hexanol, the solvent used in sol-gel systems. The absorbance was measured at 1925 μ on a series of sol-gel column samples which were previously analyzed by gas chromatography. The data are presented in Table 9.

Table 9

RESULTS OF ANALYSIS FOR WATER CONTENT

<u>Sample</u>	<u>Water Content by Gas Chromatography (%)</u>	<u>Absorbance</u>
Reference	0.12	0.0 (blank)
# 9	0.57	16.7
# 50	0.61	16.5
# 15	0.70	21.1
# 17	0.86	28.5
# 5	1.22	43.3
#500	2.70	99.5

A straight line was obtained when the water concentration was plotted versus absorbance, indicating the technique was feasible. The water concentration was reduced in the blank or reference solution from 0.12% to 0.07% by removal of the water by distillation. (H. A. Woltermann, J. Y. Jarvis, T. L. Ulrick and W. R. Amos)

SPECTROPHOTOMETRIC DETERMINATION OF THORIUM IN THE PRESENCE OF URANIUM USING ARSENAZO-III

The purpose of this investigation was to develop a method for the determination of trace quantities of thorium in samples containing uranium.

The use of arsenazo-III in the spectrophotometric determination of several elements has been reviewed by Savvin.^{25,26} Thorium, uranium, zirconium and hafnium in the tetravalent oxidation state form strongly absorbing complexes with arsenazo-III in 1-10M HCl solutions. Sensitivities of about 0.1 $\mu\text{g/ml}$ can be attained in 1-cm cells at 665 m μ .²⁶ The solution to be analyzed must have the oxidizing and reducing agents removed since they could decompose the arsenazo-III.²⁶ It was also stated that the elements could be determined in the presence of complex-forming anions such as sulfates, fluorides, phosphates and oxalates.²⁶

It was the purpose of this investigation to develop a method for the determination of microgram amounts of thorium in samples containing uranium. Although uranium(IV) also forms a strongly absorbing complex with arsenazo-III, it was reported that six times as much UO_2^{2+} as Th^{4+} could be tolerated in a thorium determination.²⁶ It was found in this investigation that up to four times as much uranium in a sample 1.5M in HNO_3 did not considerably affect the thorium analysis. For samples containing large amounts of uranium, this element was removed from a thorium-containing sample by anion exchange in HCl. In strong HCl solutions, uranium(IV or VI) is strongly adsorbed while thorium shows no adsorption on anion exchange resin at any HCl concentration.²⁷

The method described here has been applied to two different types of samples. First of all, the method was applied to the determination of trace amounts of thorium in uranium phosphite compounds. In this analysis, it was necessary to separate the uranium from the thorium. These samples were dissolved and diluted with 10M HCl, and an aliquot containing about 20 μg of thorium was taken for analysis. A few drops of 30% H_2O_2 were added and the sample was heated to decompose the excess H_2O_2 . After cooling, the sample was passed over a 1.5-cm diameter by 12.5-cm long column of Bio-Rad AG-1X4 anion exchange resin (50-100 mesh) previously washed with 10M HCl. Complete removal of the thorium was accomplished by elution with four column volumes of 10M HCl. The samples were then evaporated to a volume of about 10 ml before colorimetric analysis for thorium was performed.

The second type of sample analyzed was waste solutions containing small amounts of both uranium and thorium in 0.5-1.4M HNO_3 . These solutions were analyzed without a chemical separation and usually without removing the HNO_3 . An aliquot containing about 20 μg of thorium was transferred to a 25-ml volumetric flask, 4 ml of the arsenazo-III reagent was added, and the sample was diluted to volume with 10M HCl. The arsenazo-III reagent was prepared by dissolving 0.50 g of 1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-phenylarsonic acid] (J. T. Baker) in a 50/450 ml solution of ethanol/deionized water, and filtering. After

15 min for color development, the absorbance at 665 m μ was measured relative to a reagent blank prepared in the same manner but omitting the sample. From this absorbance, the thorium content of the sample was determined from a standard curve. This standard curve was obtained from data on an 8.85- μ g/ml standard thorium solution prepared by dissolving Fisher-purified ThO₂ in HNO₃.

A standard curve for the spectrophotometric determination of thorium with arsenazo-III is shown in Figure 7. The calculated molar extinction coefficient from the data is 114,600 liter/mole-cm. Molar extinction coefficients calculated from two other standard curves prepared with different arsenazo-III solutions were 120,000 and 123,000 liter/mole-cm. These values compare favorably with previously reported molar extinction coefficients of 130,000²⁶ and 120,000 liter/mole-cm.²⁸ The variation in this extinction coefficient emphasizes the need for preparing a new standard curve when a new arsenazo-III solution is prepared.

The second type of sample analyzed contained uranium and aluminum in addition to thorium in dilute HNO₃. Thus, it was desired to determine the effects of these substances on the determination of thorium when no chemical separation or acid fuming was performed prior to analysis. Results given in Table 10 indicate little interference from small amounts of HNO₃ and aluminum. Likewise, four times as much uranium (in HNO₃) as thorium shows little effect on the thorium determination. It has been previously reported that six times as much UO₂²⁺ as Th⁴⁺ would not interfere.²⁶ Likewise, large amounts of iron(III), lead, cobalt, calcium,

FIGURE 7 - Standard curve for determination of thorium with arsenazo-III.

Table 10

INTERFERENCE STUDIES IN THE SPECTROPHOTOMETRIC
DETERMINATION OF THORIUM WITH ARSENAZO-III

Sample	Aliquot Analyzed (ml)	HNO ₃ Concentration (M)	Aluminum Present (μg)	Uranium Present (μg)	Thorium Found ^a (μg)
1A	0.250	1.5	20	5	22.3
1B	0.250	1.5	20	5	21.9
2A	0.250	0.8	10	1	22.8
2B	0.250	0.8	10	1	22.2
3A	0.100	1.5	20	25	23.0
3B	0.100	1.5	20	25	23.0
4A	0.100	1.5	20	100	23.8
4B	0.100	1.5	20	100	23.7

^aEach sample contained 22.1 μg of thorium.

aluminum, nickel, chromium, titanium and rare earths have been reported as causing no interference in the determination of thorium with arsenazo-III.²⁶ It has also been reported that zirconium interference can be removed by complexing with oxalic acid.²⁵

This method should also be applicable to the determination of thorium in plutonium since the latter would be removed on an anion exchange column from 10M HCl if the plutonium were in the tetrapositive oxidation state.²⁷ (C. T. Bishop, E. B. Nunn, P. L. Redding and W. G. Yates)

STRUCTURE DETERMINATION OF CALCIUM TELLURATE
WITH X-RAY POWDER DIFFRACTION DATA

Alkaline earth metal tellurates were examined by x-ray diffraction techniques in order to determine their lattice parameters and crystal structures. Using Mound crystallographic computer programs, initial parameters were obtained from the diffraction lines on the powder pattern of Ca₃TeO₈. These preliminary parameters were then refined by the least squares method. The refined values are:

$$a = 5.448 \pm 0.004 \text{ \AA}$$

$$b = 5.613 \pm 0.005 \text{ \AA}$$

$$c = 8.008 \pm 0.008 \text{ \AA}$$

$$\beta = 90.89 \pm 0.08^\circ$$

Additionally, a sample of Ca_3TeO_6 was prepared for diffractometer analysis by combining it with a mixture of parlodian and ether alcohol to form a thin slurry which was dried on a clean microscope slide. The diffraction peaks for the sample were recorded on a strip chart by scanning the 2θ angle from 14 to 114° on a modified G.E. XRD-3 diffractometer. Using the duPont 310 curve resolver, a total of 56 integrated intensities was obtained from the 2θ scan. The preliminary lattice parameters calculated from the diffractometer tracing of Ca_3TeO_6 are:

$$a = 5.6371 \text{ \AA}$$

$$b = 5.8526 \text{ \AA}$$

$$c = 8.1057 \text{ \AA}$$

$$\beta = 90.77^\circ$$

The agreement between calculated and observed line spacings, for the diffractometer tracing and the powder pattern, is listed in Tables 11 and 12, respectively. This agreement is expressed as Q-values, where $Q = (1/d^2) \times 10^4$, in $\text{\AA}^{-2}$, and is based on a monoclinic cell.

The film data are compared with the diffractometer data in order to determine the degree of preferred orientation, if any, that may bias the data obtained with the diffractometer. Appropriate corrections are then applied.

Using both the corrected diffractometer data and the film data, three-dimensional Patterson functions have been computed. Neither function yields a trial model that can be refined to give an agreement factor below 0.40 (a fully refined model would give an agreement factor of ~ 0.15 or less). Failure to obtain a better agreement with the data indicates that only a partial solution to the structure has been forthcoming.

Owing to the similarity between the x-ray diffraction diagram of Ca_3TeO_6 and Ca_3UO_6 ,²⁷ these compounds could be considered isomorphous. However, the refinement has not been successful using the Ca_3UO_6 atomic positions as initial trial parameters for Ca_3TeO_6 .

An attempt to refine the data in a centric space group rather than the acentric case as indicated by the Patterson function will be made.

Table 11

DIFFRACTOMETER DATA FOR Ca_3TeO_8

hkl	Q_{calc}	Q_{obs}	I_o
011	444	444	65
101	461	467	52
110	607	607	86
111	765	762	13
020	1168	1174	70
112	1228	1221	285
200	1259	1265	85
210	1551	1557	7
121	1641	1649	29
$10\bar{3}$	1667	1680	17
211	1715	1711	50
$20\bar{2}$	1892	1888	6
$12\bar{2}$	2079	2061	3
122	2103	2107	8
220	2428	2458	113
023	2538	2530	26
$20\bar{3}$	2593	2591	9
$03\bar{1}$	2780	2811	5
$21\bar{3}$	2885	2882	10
130	2942	2935	14
222	3059	3076	19
131	3100	3100	95
311	3295	3330	8
302	3477	3485	5
$02\bar{4}$	3603	3596	50
$20\bar{4}$	2647	3647	42
312	3769	3778	145
$23\bar{1}$	4027	4026	7
$10\bar{5}$	4091	4093	14
321	4170	4198	31
$11\bar{5}$	4383	4374	10
$23\bar{2}$	4471	4468	10
040	4671	4738	9
224	4910	4934	42
400	5036	5034	12
205	5124	5121	8
401	5212	5217	17
304	5340	5359	15
$41\bar{1}$	5456	5448	40
$14\bar{2}$	5582	5581	8
402	5692	5686	13
$32\bar{2}$	6033	6021	8
$22\bar{5}$	6173	6183	45
225	6292	6302	21
403	6477	6467	5
026	6648	6645	10
$20\bar{6}$	6811	6794	8
$12\bar{6}$	6927	6933	19
150	7613	7614	10
511	8343	8348	8
250	8557	8570	24
207	8802	8792	27
343	8927	8925	17
$33\bar{5}$	9177	9171	33
$12\bar{8}$	11178	11172	18
600	11331	11320	18

Table 12

FILM DATA FOR Ca_3TeO_6

<u>hkl</u>	<u>Q_{calc}</u>	<u>Q_{obs}</u>
011	473	470
002	624	626
020	1268	1250
$\bar{1}21$	1755	1747
004	2498	2490
031	3010	3016
$\bar{2}13$	3116	3118
{ $\bar{3}02$	3617	3654
{302	3705	
132	3830	3819
015	4220	4258
$\bar{2}32$	4799	4792
$\bar{2}24$	5057	4992
$\bar{1}16$	6230	6230
126	7270	7288
007	7649	7653
501	8628	8613
$\bar{4}32$	8818	8812
244	8980	8981
252	9931	9944
245	10399	10383
{ $\bar{3}44$	10520	10554
{ $\bar{1}18$	10586	
$\bar{5}23$	10998	11000
523	11219	11195
$\bar{3}36$	11378	11361
$\bar{2}54$	11716	11710
610	12464	12452

(P. W. Seabaugh and R. R. Eckstein)

THORIUM DETERMINATION

A simple method of determining thorium in the presence of plutonium in thoria-plutonia solid solution fuel was tested and found to be satisfactory. In an acid solution plutonium is reduced to the trivalent state with hydroxylamine hydrochloride, and the thorium-thorin complex is formed and measured at 545 m μ .³¹ Conformity with Beer's Law was noted up to 80 μg of thorium. Although not as precise as a macrotechnique, this method allows a quick determination of thorium.

The EDTA indirect titration of thorium³¹ was used on pure thorium solution. Good precision was possible and the direct EDTA titration results agreed with the Cu^{2+} back-titration results. Because plutonium interferes quantitatively, it is necessary to either separate the plutonium and thorium or accurately determine plutonium first. (H. A. Woltermann)

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