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MOUND LABORATORY PROGRESS REPORT FOR CHEMISTRY
APRIL-JUNE, 1967

MASTER

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MONSANTO RESEARCH CORPORATION

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MIAMISBURG, OHIO

OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

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

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SUMMARY

RADIOELEMENTS

Half-Life Determination by Decaying Pairs Analysis of a set of synthetic data yielded trends similar to those found with experimental data treated by the method of decaying pairs. An equation has been derived for determining the point at which the minimum standard deviation occurs in the synthetic data, indicating that a similar solution can be found for the experimental data. The equation for the synthetic data shows the minimum standard deviation to be a simple function of the number of points and the distance along the abscissa by which the points of any pair are separated. However, the equation cannot be directly applied to the experimental data because of the difference in the method of weighting the data. (Page 9)

Residue Adsorption An aged source of radium-228, intended for use as a source of actinium-228, was purified by residue adsorption. A single separation removed 94.4% of the thorium-228; the radium-228 yield was 94% as determined from the amount of radium-226 with which it was contaminated. It is expected that a second separation will remove the residual thorium-228, but it is not certain that the radium-228 can be used as planned because of the large amount of radium-226 present. (Page 16)

Alpha-Beta Branching Ratio of Actinium-227 A series of instrumental malfunctions seriously impeded the work on the alpha-beta branching ratio of actinium-227. The computer program for processing the data was revised to allow for the substantial gain shifts which have occurred. Each spectrum is now being individually calibrated, permitting more precise definition of the areas of the alpha spectra which are to be summed. The branching ratio still appears to be approximately 1.7 - 1.8%. (Page 19)

Radiochemistry of Osmium The nuclear energy level scheme of iridium-193 has been established by studying the gamma spectroscopy associated with the beta decay of osmium-193. Additional conversion electron studies have been hampered by a lack of suitable techniques of preparing very thin deposits of osmium from aqueous solution. Several plating techniques were examined experimentally and a method selected which shows promise of providing reliable counting slides. (Page 23)

Uranium-234 Recovery An extraction facility to recover uranium-234 from plutonium-238 raffinate solutions is being fabricated. Raffinate solutions estimated to contain 2.4 g of uranium-234 have been collected in drums for storage until the extraction facility is operational. Analyses of these solutions indicated poor uranium separation in the anion exchange process. Gas evolution in stored raffinate solutions has not been a problem. (Page 24)

Thorium-229 Recovery

Solvent Extraction A third run was made to test the di-secondary butyl phenyl phosphonate - diethyl benzene method of thorium-uranium separation on a 22-g sample of uranium. The thorium was essentially completely separated from the uranium. (Page 25)

Actinium-227 Production A study is in progress on the production of actinium-227 from radium-226 by neutron irradiation in a reactor. The 17 g of radium on hand is contaminated with nickel. In the development of a purification method using barium as a non-radioactive substitute for radium and barium-133 as a tracer, the nickel contamination was best removed by precipitating the barium with a solution of 6N HCl and adding propanol to ten times the volume of HCl. The barium was re-precipitated by adjusting the water solution of barium chloride to a pH of 9.2 with NH_4OH and precipitating with carbon dioxide. Material precipitated by this method would be suitable for encapsulation and irradiation. (Page 26)

ANALYTICAL AND INSTRUMENTATION

Techniques for Measuring Internal Conversion Coefficients Methods are being developed to determine the "K" electron conversion coefficients. The area under the proper electron peak in the conversion electron spectrum of the source must be found. A correction factor, called the geometry factor, was obtained to correct for the fact that the detector "sees" only a fraction of the 4π radiation.

A study was made of the effects of source-to-detector distance, reflection, source size, and source backing material on the resolution associated with each source being studied. The results indicated that both the standards and the source to be analyzed should be prepared so that they are as similar as possible to minimize variations in the data obtained.

The method of computing accurately and consistently the NaI photopeak area for absolute gamma counting was examined. A comparison was made between results for the photopeak area obtained by the parallel-line method by planimeter measurements, the straight-line method by planimeter measurements, the straight-line method by integration of data, and valley-to-valley integration. The results indicate that errors introduced by using different area computations are significant and care should be used when photopeak areas are evaluated. (Page 28)

Crush Strength Apparatus A new crush strength apparatus which provides considerably greater resolution than the apparatus previously used was constructed. The new apparatus uses a force transducer, whose output is amplified and recorded. A larger probe to crush the microspheres has materially speeded up the measurements. (Page 32)

X-Ray Diffraction of Rubidium Uranyl Nitrate X-ray diffraction patterns of single crystals of rubidium uranyl nitrate $[\text{RbUO}_2(\text{NO}_3)_2]$ were obtained. Weissenberg photographs of rhombohedral prismatic habits indicated the crystal belongs in the rhombohedral crystal system. The nonextinctions from the Weissenberg photographs infer a rhombohedral lattice based on a hexagonal reference system. The hexagonal lattice parameters are $a = 9.38 \text{ \AA}$ and $c = 18.9 \text{ \AA}$; the rhombohedral lattice parameters are $a = 8.32 \text{ \AA}$ and $\alpha = 68.67^\circ$. The most probable space group is $R\bar{3}c$. (Page 35)

Determination of Organic Materials in Water The concentration of organic materials in water can be determined by gas chromatography using a flame ionization detector. The method involves extraction of organics from water with diethyl ether and concentration by a factor of 1000. The method permits detection of organics in water at concentrations as low as 10 ppb. (Page 35)

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RADIOELEMENTS

Basic and applied research is being conducted on a number of radioelements to determine their physical properties, to develop analytical techniques, and to study the basic radiochemistry involved. Of particular interest are alpha emitters, their decay chains, their isotopes, and their chemical homologs. Research quantities of some of these isotopes are being isolated.

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HALF-LIFE DETERMINATION BY DECAYING PAIRS

It has been shown that the determination of a half-life by pulse counting is highly sensitive to the value of the resolution time, τ , used for correcting the observed counting rate to a "true" counting rate.¹ The method of decaying pairs was developed to eliminate τ from the computations. The rationale of this procedure and the derivation of the equations used in the computations have been discussed in an earlier report.² The method has been shown repeatedly to yield half-life values comparable to those obtained by the variational and general methods,³ but usually with precision indices two to three times lower, reflecting the elimination of one of the three parameters determined.

When only one pair of sources is being counted, the computations pose no particular problem; the data yield a single half-life with its associated precision index. However, if N sources are being counted, the number of possible pairs becomes $N(N - 1)/2$, with each pair yielding its own half-life and precision index. If all of these values were truly independent,

¹H. W. Kirby and J. Z. Braun, Determination of Coincidence Corrections in a Proportional Counter, II - The Known Half-Life Method, MLM-1202 (June 1, 1964).

²J. F. Eichelberger, G. R. Grove and L. V. Jones, Mound Laboratory Progress Report for April, 1965, MLM-1254 (April 30, 1965) p.7.

³H. W. Kirby and J. Z. Braun, Determination of Coincidence Corrections in a Proportional Counter, III - Least Squares Analysis by the Variational and General Methods, MLM-1263 (September 15, 1965).

the grand mean and its external standard deviation could be routinely computed from the equation:

$$\bar{\bar{X}} = \frac{\sum w\bar{X}}{\sum w} + \sqrt{\frac{\sum w(\bar{X} - \bar{\bar{X}})^2}{R - 1}} \quad (1)$$

where $\bar{\bar{X}}$ is the grand mean, $\bar{X}$ is an intermediate mean or half-life, w is a weight inversely proportional to the square of the standard deviation of the corresponding $\bar{X}$, and R is the total number of pairs.

However, since the intermediate means are not independent, it has been assumed that the number of degrees of freedom is not $R-1$ but $N-1$. This assumption has been tested empirically³ and appears to be valid. However, some discrepancies occur which appear to be small and randomly distributed, but these have been ascribed either to truncating errors in the computations or to deviations in the experimental data, or both. The problem has not yet been solved analytically.

One approach to its solution is to generate by computer a series of random data which fit the equation of a straight line. Since the equation of a straight line is uniquely determined from any two points on the line, a situation comparable to that in the decaying pair method can be simulated by comparing the least-squares solution of the overdetermined equation with the grand mean of the solutions from all possible pairs of points.

The equation selected as a starting point was:

$$Y = 1000000 - 10000 X \quad (2)$$

Values of Y were generated on the assumption that the error distribution was Gaussian and that every value had a standard distribution, σ_y , equal to 100. The least-squares solution for 100 generated points was:

$$Y = (1000022.3 \pm 20.3) - (10000.493 \pm 0.349) X \quad (3)$$

Of the 100 points used in the solution, 49 showed negative deviations and 51 showed positive deviations from the least-squares solution. Sixty-six percent of the deviations were within one standard deviation and 95% were within two standard deviations of the least-squares solution, indicating that the data were satisfactorily random and the error distribution was Gaussian, as required. Similar results were obtained for 25, 50 and 250 generated points.

In combining the intermediate solutions from all possible pairs into a grand mean, it is necessary to take into account the standard deviations of their slopes and intercepts. Although the individual points were defined as having identical standard deviations and, therefore, identical

weights, the standard deviations of the intermediate solutions are found, by the propagation of errors,⁴ to be functions of the values along the abscissa. The weights are taken to be inversely proportional to the squares of the standard deviations. On this basis,

$$w_{ij}(B) = \frac{(X_j - X_i)^2}{2\sigma_y^2} \quad (4)$$

$$w_{ij}(A) = \frac{(X_j - X_i)^2}{\sigma_y^2 (X_j^2 + X_i^2)} \quad (5)$$

where $w_{ij}(B)$ and $w_{ij}(A)$ are the weights of the slope and intercept, respectively, X_j and X_i are the corresponding values along the abscissa, and σ_y is the assumed constant standard deviation of each data point. Combining all 4950 possible pairs by Equation 1 yields:

$$Y = (999998.56 \pm 2.45) - (10003.660 \pm 0.067) X \quad (6)$$

The standard deviation of the intercept in Equation 6 is smaller than that of Equation 3 by a factor of 8.3; the ratio of their respective slopes is 5.2. If the term $R-1$ in Equation 1 is replaced by $N-1$, the standard deviations in Equation 6 become ± 17.32 and ± 0.474 , respectively, which are in considerably better agreement with the corresponding least-squares values. The ratios of the standard deviations are 0.85 and 1.36 for the intercept and slope, respectively.

However, since these solutions are derived from perfectly random data, involving no systematic errors and no assumptions regarding instrumental characteristics, such as resolution time, nearly perfect agreement would be expected for a large sampling.

Since the data in the previous computations were correlated, it would be useful to know whether the discrepancy would be eliminated if the data were uncorrelated. To reduce the degree of correlation, each data point, in turn, was used as a reference point, or "standard", for pairing with all other points. A sampling of the results is given in Table 1, which also includes, for comparison, those obtained with all 4950 pairs. It does not appear that the agreement is significantly improved by reducing the degree of correlation in this manner.

In the preceding study, the correlation was reduced but not eliminated, since all pairs in any one solution were correlated through the point

⁴A. G. Worthing and J. Geffner, Treatment of Experimental Data, New York, John Wiley and Sons, 1943, p. 205.

Table 1

COMPARISON OF LEAST-SQUARES* AND PAIRED DATA SOLUTIONS USING ONE POINT AS REFERENCE

Reference Point	ΔInt^b	$\sigma(\text{Int})$	ΔSlope^c	$\sigma(\text{Slope})$	Ratio of Standard Deviation ^d	
					Intercept	Slope
1	+ 20.2	0.32	-3.03	0.250	63.07	1.39
6	+ 43.4	1.16	-0.77	0.196	17.46	1.77
11	- 56.1	2.26	+0.82	0.214	8.96	1.63
16	-127.1	5.073	+3.07	0.340	3.99	1.02
21	- 22.7	5.078	+0.32	0.245	3.99	1.42
26	-266.8	10.68	+3.18	0.459	1.90	0.76
31	+ 22.7	8.37	+0.20	0.291	2.42	1.20
36	- 3.0	10.20	+0.03	0.311	1.98	1.12
41	+ 18.6	18.92	-1.35	0.532	1.07	0.65
46	-120.5	19.99	+0.55	0.495	1.01	0.70
51	72.2	19.01	+0.05	0.436	1.07	0.80
56	+118.5	35.89	+0.20	0.714	0.56	0.49
61	+ 9.4	19.17	+0.51	0.340	1.06	1.02
66	- 1.7	18.32	-0.10	0.312	1.11	1.12
71	+ 13.4	22.80	-1.33	0.357	0.89	0.98
76	+ 24.9	20.40	-1.25	0.308	0.99	1.13
81	+ 22.8	16.88	-1.14	0.259	1.20	1.35
86	+ 25.0	16.46	-1.09	0.234	1.23	1.49
91	+ 15.3	15.84	-0.65	0.206	1.28	1.69
96	- 55.0	17.25	+1.56	0.216	1.17	1.62
All Possible Pairs	- 17.3	16.42	+3.17	0.474	0.85	1.36

*Least Squares Solution: $Y = (1000022.3 \pm 20.3) - (10000.493 \pm 0.349) X$

^bWeighted grand mean of intercept by pairs minus least-squares intercept.

^cWeighted grand mean of slope by pairs minus least-squares slope.

^dRatio of least-squares standard deviation to weighted grand mean standard deviation.

used as reference. The correlation can be completely eliminated by dividing the data in two parts and pairing each data point of one set with only one data point in the other. (This is the technique used when the decaying pair method is applied to the decay of a single source.⁵) A convenient method for grouping the data is to divide them into odd- and even-numbered observations. The same grouping can be used repeatedly for various values of ΔX , the distance along the abscissa by which the two points of any pair are separated. As the value of ΔX increases the number of possible pairs decreases, so that 100 points would yield 50 pairs with $\Delta X = 1$, 25 pairs with $\Delta X = 51$ and only one pair with $\Delta X = 99$. For each ΔX the data are uncorrelated, since no data point is used more than once, and the weighted average of all the solutions can be determined directly from Equation 1.

When the results are plotted (Figure 1), they show a striking resemblance to those obtained with experimental data treated by the method of decaying pairs (e.g., Figure 1 of Reference 5). The resemblance is the more remarkable in that each of the experimental solutions was a linear least-squares fit and not, as in the present case, a weighted average of results derived from pairs of synthetically generated random data.

FIGURE 1 - Weighted Average Slope by Pairs for 100 Synthetic Points (Error Bars = $\pm \sigma$).

⁵Mound Laboratory Quarterly Progress Report: July-September, 1966, MLM-1388 (September 30, 1966) p. 7.

It was stated in the earlier report⁵ that the probable errors pass through a minimum value, with the smallest probable error in that set of solutions occurring at 3750 sec. The standard deviations of the synthetic data also pass through a minimum; their reciprocals (multiplied by the least-squares standard deviation) are plotted in Figure 2 as a function of ΔX . If a smooth curve is drawn through these points, the maximum (corresponding to the minimum standard deviation) occurs at $\Delta X = 67$, for which the number of pairs available from 100 points is 20.

FIGURE 2 - Reciprocal Standard Deviation (Pairs) as a Function of ΔX .

The location of this maximum can be shown to be a function of ΔX and the number of pairs, R , as follows:

For a single pair, the standard deviation of the slope is given by

$$\sigma_B = \sqrt{\frac{\sigma_{Y_1}^2 + \sigma_{Y_2}^2}{(X_1 - X_2)^2}} \quad (7)$$

and, since the standard deviations of all the data points were set equal,

$$\sigma_B = \frac{\sigma_{y1} \sqrt{2}}{\Delta X} \quad (8)$$

The weighted average of all slopes with constant ΔX and the weights defined by Equation 4 has an external standard deviation given by:

$$\sigma_{ext} = \sqrt{\frac{\sum w_i (\bar{B} - B_i)^2}{(R - 1) \sum w_i}} \quad (9)$$

and, since all the weights are equal for constant ΔX , the external standard deviation of the mean is

$$\sigma_{ext} = \sqrt{\frac{\sum d_i^2}{(R - 1)R}} \quad (10)$$

If, as a first approximation, it is assumed that, on the average, the individual deviations are equal to their standard deviations, Equation 10 reduces to

$$\sigma_{ext} = \frac{\sigma_y}{\Delta X} \sqrt{\frac{2}{R - 1}} \quad (11)$$

For a given number of data points, N , and a particular ΔX , the number of possible pairs is

$$R = \frac{1}{2} (N - \Delta X + 1) \quad (12)$$

Replacing R in Equation 11 by this expression and taking reciprocals yields

$$\frac{1}{\sigma_{ext}} = \frac{\Delta X (N + 1 - \Delta X)^{1/2}}{2\sigma_y} \quad (13)$$

If Equation 13 is differentiated with respect to ΔX and the derivative is set equal to zero, the point at which the standard deviation will be a minimum is defined by

$$\Delta X = \frac{2}{3} (N + 1) \quad (14)$$

In the present instance, for $N = 100$, the minimum standard deviation should (and does) occur at $\Delta X = 67$.

Equations 13 and 14 cannot be applied directly to experimental data obtained by the method of decaying pairs because each of the intermediate half-life values is obtained from a least-squares solution of

the expression:²

$$\ln\left(\frac{1}{n} - \frac{1}{m}\right) = \lambda t + \text{Constant} \quad (15)$$

and because the weights applied to the observations are considerably more complex than those being used with the synthetic data. However, the reciprocal probable errors exhibit a trend similar in appearance to the trend for the simpler case (Figure 3), and it is expected that an equation comparable to Equation 13 will be derived for the experimental data. (H. W. Kirby and R. H. Howell)

FIGURE 3 - Reciprocal Probable Error (Least Squares) for the Half-Life of Lead-211 by Decaying Pairs (271 Observations).

RESIDUE ADSORPTION

Preliminary work on the separation of actinium from thorium by residue adsorption was described in the previous report.⁶ Ideally, quantitative data should be obtained for the adsorption of each of these elements

⁶Mound Laboratory Progress Report for Chemistry: January-March, 1967, MLM-1405 (March 31, 1967) p. 13.

individually, in the absence of the other. However, the low alpha-to-beta branching ratio of actinium-227, its complex decay chain and the absence of distinctive gamma energy peaks combine to make its quantification extremely difficult.⁷ Actinium-228, the 6.13-hr daughter of 5.75-yr radium-228 (mesothorium) is a more attractive isotope for this purpose. Actinium-228 has a useful gamma spectrum⁷ and the growth of its long-lived daughter (1.91-yr thorium-228) does not significantly interfere with its quantification. Consequently, a sample of radium-228 was obtained for use as a "cow" from which actinium-228 could be frequently "milked."

A gamma spectrum of the radium-228 stock solution showed the presence of radium-224, hence that of thorium-228, indicating that the source would have to be purified before it could be used for the recovery of actinium-228. A more serious form of contamination was revealed when an alpha spectrum was run; the one-millicurie source of radium-228 contained approximately one milligram (one millicurie) of radium-226 (Figure 4). Nevertheless, the purification was performed, since no other source of radium was immediately available.

FIGURE 4 - Alpha Spectrum of Original Mixture of Radium-226 and -228 (Reignited to Minimize Radon-222 Interference).

⁷H. W. Kirby, "The Analytical Chemistry of Actinium," Progress in Nuclear Energy, Series IX, Vol. 8, Part 1, 1967, p. 89-139.

The stock solution was evaporated to dryness in a Pyrex beaker, redissolved in dilute HNO_3 and again evaporated to dryness. The residue was cooled and leached with 3M NH_4OH . The ammoniacal desorbate was passed through a coarse glass wool filter to assist in the removal of colloidal particles. An alpha spectrum of the desorbate showed no identifiable thorium-228; however, interference from the 5.486-Mev alpha peak of radon-222 would mask the thorium-228 if it were present in trace amounts. The ammoniacal residue in the beaker and on the glass wool filter was redissolved; an alpha spectrum showed that it contained nearly all of the original thorium-228. Samples of both fractions were set aside for 55 days to allow the radium-224 to decay (or grow) to equilibrium with the thorium-228. Since radon-222 and its decay products had now grown to equilibrium with the radium-226, the samples were reignited to drive off most of the radon isotopes and short-lived decay products. The alpha spectra (Figures 5 and 6) showed that the adsorbate contained 94.4% of the thorium-228 and 6.0% of the radium-226.

FIGURE 5 - Alpha Spectrum of Ammoniacal Desorbate (Reignited to Minimize Radon-222 Interference).

FIGURE 6 - Alpha Spectrum of Ammoniacal Residue
(Reignited to Minimize Radon-222 Interference).

The desorbate, containing 94% of the radium isotopes, will be repurified to remove the residual thorium-228. It is expected that, when this purification has been completed, less than 0.5% of the thorium-228 will remain with the radium-228 and this small amount should not significantly interfere with the quantification of the actinium-228. (H. W. Kirby and K. Muldoon)

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ALPHA-BETA BRANCHING RATIO OF ACTINIUM-227

During the past quarter a series of instrumental malfunctions and uncontrolled line voltage fluctuations interfered with the work on the alpha-beta branching ratio of actinium-227. Since the analytical technique described in the previous report⁶ depends heavily on a high degree of resolution and instrument stability, it has not been possible to proceed as rapidly as had been expected.

The technique being used consists of separating radium-223 quantitatively from actinium-227 and thorium-227 by the method of residue adsorption and comparing the areas under the actinium-227 and thorium-227 alpha peaks in a series of spectra obtained over a period of several days to a week. Removal of the radium-223 minimizes the decay product contribution to

these peaks but cannot completely eliminate them, since radium-223 and its decay products begin to grow back as soon as they are removed. Correction for this growth is made by determining the area under the polonium-215 peak (7.38 Mev) in each spectrum and determining, by the method of least squares, the counting rates of actinium-227 and thorium-227 which would have been observed in the absence of the decay products.

The problems have manifested themselves in essentially two ways: by the appearance of double peaks in some of the spectra, indicative of abrupt gain shifts, and by gradual drifting of the spectra over a period of several hours, probably due to a more gradual gain and baseline shift.

A number of components in the spectrometer system were found to be in marginal condition and were replaced, but the drifting continued. The incoming line voltage was also found to be somewhat erratic, and a Sola constant voltage transformer was installed. This addition to the system appeared, for a time, to have eliminated the problem, but the drifting and double-peaking have reappeared intermittently.

There is little that can be done mathematically to correct for the abrupt shifting which causes double peaking, but the slow drift can be compensated for by calibrating each spectrum individually, instead of relying on a single initial calibration with americium-241. To accomplish this, the IBM S/360 computer has been programmed to search for the 7.38-Mev peak of polonium-215. With this peak as a starting point, the computer then finds the 6.036-Mev peak of thorium-227 (or, if a radium-223 spectrum is being analyzed, the radon-219 peak at 6.813 Mev). From these two known peaks the baseline and channel width are recomputed and the spectrum is recalibrated. Peak area summations are then based upon specific energy limits rather than on channel numbers predetermined from the initial calibration. When the data were again analyzed with this modification it was found that, even in spectra which exhibited no obvious peak shifts, some fluctuation had occurred which required recalibration.

In addition to the change in calibration procedure, the analytical computations were extended. In the previous report, equations were derived which used the polonium-215 peak as an indicator of the amount of radium-223 interference in the actinium-227 and thorium-227 peak areas. It was shown that the thorium-227 peak area computed by least squares agreed with an independent direct measurement of a portion of the thorium-227 spectra which had no radium-223 interference. The computer was therefore programmed to determine directly the total amount of radium-223 in each spectrum, using the direct thorium-227 peak area count as a guide to the amount of thorium-227 overlapping the radium-223 spectrum. This modification made it possible to determine independently the amount of radium-223 "tail" in the actinium-227 region, instead of relying solely

on an indirect measurement based on the polonium-215 peak. The results obtained by these two methods of computation were in good agreement (Table 2), except when drifting was so severe that part or all of the polonium-215 peak was lost from the spectrum. This agreement served as further confirmation of the assumptions upon which the least-squares analysis was based.

It had been assumed that, since over 99% of the actinium-227 alpha energies are above 4.728 Mev,^a a summation of the counts in the range from 4.70 to 5.00 Mev would adequately represent the total actinium-227 spectrum. It was found, however, that a significantly higher actinium-227 counting rate (and, consequently, a higher branching ratio) was computed when the lower limit was extended to 4.60 Mev (Table 2). Further extension of the summation range to 4.50 Mev yielded even higher values of actinium-227. It is not yet certain how this problem will be resolved since it probably results from the inherently poorer resolution characteristic of the alpha spectra of long-lived nuclides. In the case of actinium-227, the specific alpha activity is equivalent to that of a pure alpha-emitter whose half-life is greater than 1000 yr.

The data in Table 2 illustrate one additional point, namely, that little is gained by continuing to obtain spectra from samples which contain more than a few percent of the original radium-223, either because of poor separation (as in the case of samples #318413 and 318436) or because of regrowth. In all such cases, the probable errors of the determinations are so high as to make the results essentially useless. In the case of sample #318414, which was counted 5 days after separation, the data yielded satisfactory probable errors only because each spectrum represented 6 hr of data accumulation. In view of the instability now being experienced, such lengthy counting periods do not appear to be either feasible or desirable.

The unfortunate series of instrumental problems has not been without some benefits, for the new calibration procedure now makes it possible to assign more precise energy limits for the peak area summations instead of allowing for a small, but undetermined, amount of instrumental "jitter" and drift.

In computing the actinium-227/thorium-227 ratio as a measure of the branching ratio of actinium-227, it is assumed that no significant amount of either of these nuclides is removed when the radium-223 is separated by residue adsorption. The thorium-227 distribution can be determined immediately by comparing the counting rates of the two fractions in the 5.9-6.1 Mev range. Alternatively, the amount of thorium-227 in the

^aG. I. Novikova, E. A. Volkova, L. L. Gol'din, D. M. Ziv and E. F. Tretyakov, Sov. Phys. JETP, 10, No. 4, 663 (1960).

Table 2

BRANCHING RATIO OF ACTINIUM - COMPARISON OF COMPUTATION METHODS

Sample No.	Time after Separation (days)	$\text{Ac}^{227}/\text{Th}^{227}$ (%) ^{a, b}	$\text{Ac}^{227}/\text{Th}^{227}$ (%) ^{a, c}	$\text{Ac}^{227}/\text{Th}^{227}$ (%) ^{c, d}
318414	0	1.781 $\pm$ 0.025	1.770 $\pm$ 0.020	1.875 $\pm$ 0.021
318411	0	1.727 $\pm$ 0.028	1.724 $\pm$ 0.031	1.852 $\pm$ 0.035
318411	1	1.736 $\pm$ 0.030	1.741 $\pm$ 0.031	1.868 $\pm$ 0.033
318412	0	1.789 $\pm$ 0.012	1.791 $\pm$ 0.012	1.906 $\pm$ 0.013
318413 ^e	0	1.519 $\pm$ 0.248	1.559 $\pm$ 0.195	1.676 $\pm$ 0.213
318414	0	1.824 $\pm$ 0.055	1.804 $\pm$ 0.055	1.956 $\pm$ 0.059
318414	1	1.800 $\pm$ 0.013	1.800 $\pm$ 0.014	1.901 $\pm$ 0.014
318414	4	1.980 $\pm$ 0.188	1.955 $\pm$ 0.152	2.030 $\pm$ 0.157
318414	5	1.672 $\pm$ 0.080	1.678 $\pm$ 0.063	1.849 $\pm$ 0.060
318430	2	1.826 $\pm$ 0.024	1.827 $\pm$ 0.023	1.969 $\pm$ 0.027
318434	0	1.888 $\pm$ 0.044	1.892 $\pm$ 0.051	2.028 $\pm$ 0.054
318434	1	1.945 $\pm$ 0.089	1.936 $\pm$ 0.090	2.014 $\pm$ 0.090
318434	2	1.968 $\pm$ 0.517	2.110 $\pm$ 0.492	2.223 $\pm$ 0.499
318435	0	1.773 $\pm$ 0.023	1.767 $\pm$ 0.028	1.914 $\pm$ 0.033
318435	1	1.533 $\pm$ 0.067	1.549 $\pm$ 0.068	1.683 $\pm$ 0.064
318435	2	1.829 $\pm$ 0.037	1.855 $\pm$ 0.045	1.961 $\pm$ 0.046
318436 ^e	0	1.214 $\pm$ 0.355	1.465 $\pm$ 0.246	1.498 $\pm$ 0.287
318437	0	1.659 $\pm$ 0.041	1.684 $\pm$ 0.048	1.745 $\pm$ 0.050
318437	1	1.542 $\pm$ 0.069	1.545 $\pm$ 0.073	1.566 $\pm$ 0.083

^a Actinium-227 energy range summed - 4.7-5.0 Mev^b Radium-223 interference computed from polonium-215 area summation^c Radium-223 interference computed from radium-223 area summation^d Actinium-227 energy range summed - 4.6-5.0 Mev^e Poor separation; over 25% of radium-223 remained in actinium-227/thorium-227 fraction

adsorbed fraction can be compared with that in a standard sample of actinium-227 in equilibrium with its decay products. This type of analysis is now being done routinely, and it is found that the thorium-227 loss is consistently less than 5% and usually less than 3% of the original amount present.

On the other hand, the actinium-227 losses can be determined with accuracy only when the fractions have grown to equilibrium - approximately 6 months after separation. Several of the earlier separated fractions have now reached equilibrium; in all cases the actinium-227 loss was less than 2%, based on gross alpha counting. (H. W. Kirby and K. Muldoon)

RADIOCHEMISTRY OF OSMIUM

A considerable portion of the nuclear level scheme of iridium-193 has been worked out from gamma-ray spectroscopy of osmium-193. However, conversion electron studies to determine gamma-ray multi-polarities have been hindered by source preparation problems, since there are no osmium compounds which can be conveniently prepared by simple evaporation techniques. Therefore, a method for plating osmium metal from aqueous solution was developed.

Several samples of the separated nuclide osmium-192 were prepared for neutron activation. Following activation, the neutron capture product, osmium-193, decays to iridium-193 with a half-life of 31 hr. Conversion electrons from transitions in iridium-193 were studied with a high-resolution beta spectrometer using sources prepared by the plating technique described below. The resolution obtained with these sources is about a factor of two better than any previously reported data. The sources were prepared as follows:

- (1) The osmium-192 metal was dissolved in concentrated HNO_3 in a stream of air, producing OsO_4 (osmium tetroxide). The highly volatile OsO_4 was distilled into a centrifuge tube containing 6M NaOH cooled to 0°C .
- (2) The NaOH solution was diluted with an equal volume of a buffered plating solution containing 20 g $(\text{NH}_4)_2\text{HPO}_4$, 90 g $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and 5 g NaCl per liter of solution and was placed in a Teflon plating cell. (The plating solution recipe was provided by R. H. Price of McMaster University, Hamilton, Ontario, Canada.)
- (3) The plating cell was fitted with a 0.0002-in. nickel foil cathode and a rotating platinum anode. A current of approximately 5 milliamp at 2.5 v was required to plate osmium metal on the nickel. (R. C. Lange)

URANIUM-234 RECOVERY

Mound Laboratory is recovering uranium-234 from aged plutonium-238 by two methods. The first method,⁹ used for laboratory-scale processing, consists of an initial separation of the plutonium by anion exchange in HNO_3 , followed by hexone extraction to further purify the uranium, and a final anion exchange in both HNO_3 and HCl to remove the last traces of impurities. A second process¹⁰ uses TOPO (tri-n-octylphosphine oxide) extraction to recover and concentrate both uranium and plutonium from large-volume, low-level ion exchange raffinate solutions, followed by separation and purification of the uranium.

A uranium-234 solvent extraction recovery facility is being constructed, which will use the TOPO process to recover and concentrate uranium-234 from the waste solutions resulting from the plutonium-238 scrap recovery process. Waste solutions especially rich in uranium-234 (estimated 20-50 g) are presently being generated by the plutonium-238 scrap recovery system. To avoid the irrevocable loss of this material, selected raffinate solutions are being collected and stored in doubly contained, plastic-lined drums. Nearly 700 liters of solution (containing an estimated 2.4 g of uranium-234) have been collected in eight drums. These solutions will be stored until the uranium-234 solvent extraction facility is operational.

Various process and waste solutions have been analyzed for uranium by the TOPO-PAN method¹¹ to determine the potential quantity of uranium-234 and the uranium separation efficiency of the plutonium recovery system. From the limited amount of data, to date, it appears that in some cases the amount of uranium present may exceed the amount calculated from the decay of the plutonium-238. One small batch, containing 1.65 g of plutonium-238, was found to contain 0.45 g (26%) uranium. A possible explanation is that this material consisted of previous ion exchange raffinates which had been evaporated, thereby increasing the uranium-234 concentration. Of course, the sample could have been contaminated with another uranium isotope (e.g., uranium-238), but the history of the sample essentially ruled out this second explanation.

A second conclusion, based on the available data, is that a considerable fraction of the uranium is not appearing in the raffinate. The first

⁹P. E. Figgins and R. J. Belardinelli, J. Inorg. Nuclear Chem., **28**, 2193 (1966).

¹⁰J. F. Eichelberger, G. R. Grove and L. V. Jones, Mound Laboratory Quarterly Progress Report: January-March, 1966, MLM-1325 (March 31, 1966) p. 50.

¹¹R. J. Baltisberger, Anal. Chem., **36**, 2369 (1964).

indications of this possibility occurred when analyzed raffinate solutions were found to contain only 30 to 50% of the uranium calculated to be present from the decay of plutonium-238. When feed, plutonium product, and raffinate solutions from a single ion exchange run were analyzed, the feed solution was found to contain 2.57 g of uranium in 105 g of plutonium-238, or 2.45% uranium. (This would correspond to plutonium-238 which had aged 3.3 yr.) The plutonium product contained 0.38 g or 15% of the original uranium, and two raffinate solutions contained a total of 1.52 g or 59% of the original uranium. The difference, 0.67 g or 26%, may have been in two wash solutions which were not analyzed, or might be partially due to errors in the analyses. Additional solutions are being analyzed to obtain more data. Poor separation of the uranium from plutonium on an anion exchange column has been observed earlier⁹ in laboratory-scale work, where ten column volumes of wash solution were required to remove at least 90% of the uranium. The loss of uranium is compounded when, as sometimes happens, the plutonium content of the raffinate solution exceeds the limits for disposal, and it is necessary to reprocess this "hot" raffinate on a second ion exchange column.

At this point, it appears that the estimate of 20 to 50 g of uranium-234 in the materials currently being processed is still a valid estimate; however, a considerable fraction of this uranium-234 may be "lost" during the ion exchange processing.

Gas evolution during the storage of the uranium-234-rich raffinate solutions is being evaluated. Samples of raffinate solution were placed in a container connected to a simple U-tube manometer and the pressure of the generated gas was observed. The first solution showed a total evolution of 7.33 cc of gas per liter of solution over a period of eight weeks. At the end of the observation period, gas evolution had essentially ceased. A second raffinate solution was observed over a period of ten weeks with a gas evolution rate of 6-7 cc of gas per liter of solution per day, with no apparent decrease in the rate. This gas presumably is being generated from the decomposition of a large amount of organic material picked up in the plutonium recovery process. The particular drum storing this raffinate solution was monitored carefully, but no problems were observed, indicating that the pressure relief devices are operating satisfactorily. (P. E. Figgins)

THORIUM-229 RECOVERY

Solvent Extraction Nine-year-old uranium oxide containing 21.58 g of nine-year-old uranium-233 (21.99 g total uranium) was dissolved in concentrated HNO_3 , evaporated to dryness, and taken up in 100 ml of 2M HNO_3 . This solution was extracted repeatedly in stirred separatory funnels with 100 ml of 10% di-secondary butyl phenyl phosphonate (DSBPP) in diethyl benzene (DEB). Between each extraction, the DSBPP was stripped

with 0.005M HNO_3 to remove the uranium. The stripping solutions were evaporated to recover the uranium. After 11 extractions all of the uranium was removed from the original 2M HNO_3 solution, leaving only thorium and thorium daughters.

The aqueous mixture of thorium and its daughters was extracted with 0.1M tri-n-octylphosphine oxide (TOPO) in DEB to separate the thorium from its daughters, as well as from any other impurities which may have been present in the original sample. The TOPO-DEB was then stripped with 0.5M oxalic acid to remove the thorium. The oxalic acid solution (actually a colloidal suspension of thorium oxalate) was evaporated to dryness several times with concentrated HNO_3 to decompose the oxalic acid and to obtain the thorium product as the water-soluble nitrate.

Alpha spectrometry and alpha counting were used to monitor the procedure. Complete removal of the uranium from the thorium, resulting in a radio-chemically pure thorium product, was indicated. (M. R. Hertz)

ACTINIUM-227 PRODUCTION

A study is in progress on the production of actinium-227 from radium-226 by irradiation in a suitable reactor.

Approximately 17 g of radium are being stored in a hot cell. The radium, as the chloride salt, is contaminated with an unknown amount of nickel. The radium must be separated from the nickel, precipitated as the carbonate, sealed in suitable capsules, irradiated, and the products analyzed to study the production rate of actinium.

Two methods of purifying the radium were studied successfully. Barium was used as a non-radioactive substitute for radium and was precipitated from the soluble nickel as the chloride. In one method the barium-nickel solution was made 10.5N with respect to the HCl content. In the other method the barium was separated from the nickel by making the solution 6N with respect to HCl and adding propanol to ten times the volume of the HCl. Both filtrates passed the sulfate ion test, which indicated that the barium was completely precipitated. Washing the precipitate with three small volumes of concentrated HCl apparently removed all traces of the nickel impurity. When barium-133 was received for use as a gamma tracer, both types of separations were repeated several times using the barium-133. The 6N HCl-propanol separation gave an average loss of barium to the filtrate of 0.57%, while the 10.5N HCl separation gave an average loss of 1.39%.

The barium chloride precipitate is readily dissolved in hot water. The water solution is adjusted to pH of 9.5 with ammonium hydroxide and the barium is precipitated as the carbonate¹² by bubbling carbon dioxide through the solution for 30 min. This filtrate also gave a negative sulfate test for barium. (R. M. Watrous)

¹²H. Teicher, Precipitation of Barium Carbonate, MLM-931 (December 16, 1953).

ANALYTICAL AND INSTRUMENTATION

Methods of analyzing elements and compounds are being developed to support the programs at Mound Laboratory. These methods include instrumental techniques and standard wet methods.

TECHNIQUES FOR MEASURING INTERNAL CONVERSION COEFFICIENTS

In the technique being used to determine the "K" electron conversion coefficients, it is necessary to determine the absolute number of conversion electrons emitted from the source. One step in this process is to find the area under the proper electron peak in the conversion electron spectrum of the source. In the case of protactinium-231 the lower-energy electron peaks are complicated by the contributions of the low-energy tails of the higher-energy electrons. This complication can be eliminated by subtracting the contributions from all of the higher-energy electrons. It was found that at least over the electron energy range of 0.166 to 1 Mev there was a constant ratio of peak height to "low-energy tail" height. With this relationship it is then possible to start at the electron peak of highest energy in the spectrum and, peak by peak, to remove this contribution of each of the higher-energy peaks. This method was utilized on electron peaks of known area and was found to be very satisfactory both in reproducibility and accuracy. This technique was also checked to assure that it was not dependent on the gain of the analyzer.

In order to convert the area under the electron peak to an absolute number of electrons emitted from the source, a correction factor must be applied to account for the fact that the detector "sees" only a fraction of the total 4π radiation. This factor, called the geometry factor, was found by taking conversion electron spectra of several sources of known activities and conversion coefficients.

The ratio of the area under the electron peak to the calculated conversion electron emission rate (from $\alpha_k = N_e/N_\gamma$) gives the needed geometry factor. After several such measurements were made it was noticed that there were discrepancies in the value of the geometry factor. It was thought that these were caused by the variations in the resolution associated with each source. Several other conversion electron standards were analyzed to determine the relationship, if any, between

geometry factor and resolution. The result was that no clear relationship could be established because of other variables involved. The sources in use at the time not only varied in characteristic resolution but were of different size and on different backing material. Since the source-to-detector distance is small (about 6 mm), these variations from point sources will cause gross effects on geometry. Also, reflection toward the detector will vary with the different backings. These two variables, plus the fact that the varying resolution is caused by the two factors (different source thicknesses and densities), were enough to obscure any relationship between geometry factor and resolution. The important point gained from this study is that both the standards and the source to be analyzed should be prepared so that there is as little difference in source size and thickness as possible and that they should all be on the same kind of backing material.

The hold-down coat used was also studied. The coating of Krylon which was sprayed on the source has an appreciable electron-absorbing property. The method of spraying left no way to adequately control the thickness of Krylon. To eliminate the uncertainty the sources were coated by using an epoxy to attach a thin (approximately 0.0003 in.) layer of Mylar over the source holder. This technique proved to be satisfactory and was adopted to insure uniformity of source preparation.

In connection with the absolute gamma counting which is associated with the conversion electron work, the method of computing accurately and consistently the NaI photopeak area was examined. The absolute gamma emission rate can be expressed in terms of the counting rate associated with the photopeak area as:

$$N_0 = \frac{N_p}{T(E) \cdot P \cdot A} \quad (16)$$

where N_0 is the number of gamma rays emitted from the source, N_p is the area of the photopeak, $T(E)$ is the absolute detection efficiency, P is the value of the peak-to-total ratio, and A is a correction factor used in the presence of beta absorbers. A can be considered to be 1.0 in the present case. N_p in the equation represents the experimental area of the photopeak, but $T(E)$ and P are standard values obtained from work by Heath.¹³ It is immediately apparent that for an accurate result the configuration for which Heath obtained his values must be duplicated as precisely as possible in the present experiment. This work was done by Heath for various source-to-detector distances and source radii, each for several different detector sizes. Smooth curves were drawn for specific configurations over wide energy ranges. The present work was performed with a 3-in.-diameter by 3-in.-thick NaI(Tl) cylinder with the source located 10 cm from the face of the detector. Even if one supposes a point source which exactly satisfies the requirements for the

¹³R. L. Heath, Scintillation Spectrometry. Gamma-Ray Spectrum Catalogue, IDO-16880-1 (August, 1964).

above configuration, it cannot be assumed that the detector can be isolated from its surroundings such that only those gammas which fall within the solid angle subtended by the source and detector will be detected. Since scattered radiation will generally contribute to the count rate at an energy lower than the photopeak area, one generally only uses the area of the photopeak in the experimental determination of activity. It is for this reason that the peak-to-total ratio P must appear as a correction factor in the absolute calculation of the emission rate. This peak-to-total ratio was also determined by Heath for the energy range and configuration of interest, and it is his values again that were used for the present experimentation. It is then immediately clear that in order to accurately predict the emission rate by means of Heath's parameters, the photopeak must be computed using precisely the same definition of the photopeak area employed by Heath. Recognizing that a simple Gaussian fit to the experimental data is insufficient, Heath employs a function which is the product of a Gaussian and a polynomial:

$$Y(x) = Y_0 [1 + \alpha_1 (x-x_0)^4 + \alpha_2 (x-x_0)^{12}] \cdot \exp \left[- \frac{(x_0 - x)^2}{b_0} \right] \quad (17)$$

where $Y(x)$ is the count in channel x , x_0 is the channel at the center of the distribution, Y_0 represents the number of counts in channel x_0 , and b_0 relates to the full width at half maximum. The terms α_1 and α_2 are the parameters which determine the fit.

The photopeak area is then defined as the area obtained by fitting the experimental data to the form of Equation 17. This fit can be performed by utilizing the program developed at Oak Ridge by Helmer et al.¹⁴ A more practical method which lends itself to readily obtained data is suggested by Heath as a substitute which closely approximates the results obtained from the least-squares program. For the purposes of this discussion the approximation will be referred to as the parallel-line method.

All previous absolute counting techniques using Heath's standards were performed at this laboratory by computing the photopeak area in ways distinct from the parallel-line method. In each case it was assumed that disagreement arising from this omission would be slight. The purpose of this experiment was to determine the extent of this disagreement and to study the parallel-line method from the standpoint of consistency and reproducibility.

¹⁴R. G. Helmer, R. L. Heath, Marie Putnam and D. H. Gipson, A Non-Linear Least-Squares Program for the Determination of Parameters of Photopeaks by the Use of a Modified Gaussian Function, IDO-17015 (1964).

Figure 7 - Comparison of Methods for Calculating Areas under Photopeaks.

Figure 7 shows an example of the type of comparison made and serves as an illustration of the parallel-line method. In a single piece of data such as this, calculations of the area under the photopeak were made in the following manner:

- (a) Parallel-line method by planimeter measurement [curve (a) in Figure 7].
- (b) Straight line method¹⁵ by planimeter measurement [curve (b) in Figure 7].
- (c) Straight line method by integration of data, interpolating when necessary [curve (b) in Figure 7].
- (d) Valley-to-valley integration.

At this point a discussion is necessary about the reproducibility one can obtain using the planimeter and the consistency of the parallel-line method. The planimeter was used to measure several different curves, eight times each. In each case the percent standard deviation was computed. The average of these deviations can serve as a measure of how consistent a planimeter measurement can be. This average was found to be 0.4% which, in the light of other methods, is insignificant.

After the consistency of planimeter measurements was assured, several distinct measurements were performed on the same source, the curve to be measured was constructed in each case by the parallel-line method, and the count rate obtained from these computations was compared. This yielded a measure of the reproducibility of the parallel-line method and served as an indication of what might be expected for a standard deviation in a real case. The result was 6.5%. This apparently represents

¹⁵The straight line method simply involves constructing a triangle by connecting all points on the slopes of the photopeak curve by straight lines which intersect with one another at the peak and with the base line.

a reasonable error and one which, in an experiment such as this, is more than tolerable. It would also be interesting to compare parallel-line areas obtained by using the same data plotted on different scales. This comparison gave a difference of only 1.31%. The reproducibility of the parallel-line method is dependent on the ability to determine accurately the location of the peak channel.

After the solidarity of the parallel-line approach utilizing a planimeter was established, it was compared with the other methods of area computation listed earlier. In each case the comparison is expressed as a percent error since the parallel-line method suggested by Heath is essential for correct results. The percent error is actually an average since several curves were compared for each set of methods.

The straight line method measured by a planimeter yielded an average error of 9.3% while the straight line area obtained by integrating points gave an average error of 12.6%. The degeneration is caused by difficulties in accurate interpolation. The valley-to-valley method of simple integration of the data resulted in an average error of 28.8%.

These results indicate that in no way are the errors introduced by using different area computations trivial. Indeed they are significant and great care should be used when photopeak areas are evaluated.
(A. G. Barnett and A. R. Campbell)

CRUSH STRENGTH APPARATUS

A new crush strength apparatus which has a considerably higher resolution than the apparatus previously used was constructed. The new instrument utilizes the same hydraulic probe as the older apparatus but has the pedestal, which holds the sphere, mounted on a force transducer. The output from the transducer is amplified and the signal is displayed on a recorder. The transducer output is linear throughout its 5-kg load. The probe descends on the spheres at 0.5 cm/min.

Figure 8 shows the new apparatus. The difference between the resolution of the old and the new apparatus may be seen in Figure 9.

Figure 8 - Crush Strength Apparatus.

Old Technique

New Technique

Figure 9 - Comparison of Data Obtained with the Crush Strength Apparatus.

The determination of the crush strength of microspheres has always been a time-consuming and tedious process. The sphere was first placed on a pedestal and then its alignment with the hydraulic probe was checked with a microscope. This was necessary because of the small probe (0.0625 in.) normally used to crush the spheres. Experiments were conducted using a larger probe (0.125 in.) to determine if the crush strength varied with the size of the tip. Table 3 shows the results of crushing 500 microspheres with the two probes.

Table 3

COMPARISON OF CRUSH STRENGTH RESULTS

	Crush Strength (g)	
	Large Probe	Small Probe
Average	1903	1917
Lowest	525	550
Highest	4350	4450

The use of the larger probe increases the speed with which a determination can be made by 25-50%. In addition, the use of the larger probe with its larger area has aided in detecting the crush strength of some of the fragments from the original fracture. This result is seen in Figure 10. (N. Goldenberg)

Figure 10 - Data Illustrating Secondary Crush Strengths.

X-RAY DIFFRACTION OF RUBIDIUM URANYL NITRATE

Because some of the physical and chemical properties of uranyl and plutonyl compounds are so similar, single crystals of rubidium uranyl nitrate $[\text{RbUO}_2(\text{NO}_3)_3]$ were obtained and studied by x-ray diffraction techniques to obtain comparative data.

Weissenberg x-ray photographs of crystals of a rhombohedral prismatic habit (placed inside quartz capillaries and sealed due to the deliquescent nature of the compound) were obtained.

Rotation, zero and upper level photographs indicate that the crystal exhibits a hexagonal crystal system. The nonextinctions in the zero and upper levels are coincident with $-h+k+l = 3n$, which infers a rhombohedral lattice based on a hexagonal reference system. The hexagonal lattice parameters are: $a = 9.38 \text{ \AA}$ and $c = 18.9 \text{ \AA}$. The comparable lattice parameters based on the true rhombohedral lattice are: $a = 8.32 \text{ \AA}$ and $\alpha = 68.67^\circ$. From the known density of $\text{RbUO}_2(\text{NO}_3)_3$, two formula units were deduced for the rhombohedral unit. The space group is $\bar{R}3c$. (R. J. DeSando)

DETERMINATION OF ORGANIC MATERIALS IN WATER

The concentration of trace organic materials in water is being determined. A gas chromatographic method using a flame ionization detector was found suitable. Although many concentration techniques are reported¹⁶ in the literature, an extraction-concentration method was used in this work.

It was found that direct injection of a 1 to 2- μl water sample resulted in anomalously high values in the 300-400 ppm range independent of water treatment. This apparently is due to a "leaching" effect of water on the Porapak. Continued conditioning of the column did not reduce this background. (Injection of water is a normal technique used to reduce noise level when using a flame ionization detector.)

Although direct injection of the water sample could be useful if relatively large amounts of organics (10-100 ppm) were present, a concentration technique is necessary for small amounts. Diethyl ether was found to be a better organic solvent than carbon tetrachloride or n-hexane; not only was it more volatile and thus easier to concentrate than the other solvents but also because the solvent peak elution time was reduced from over 10 min to about 5 min. The procedure involved extraction of one liter of water sample with three 100-ml volumes of ether. The resultant 100-150 ml of ether was evaporated to 1 ml by passing argon through the solution. A distillation column was used to reduce losses of solute. Benzene added to the initial water sample served as an internal standard and as a measure of the efficiency. By

¹⁶W. B. Innes and A. J. Andreatch, Ind. Water & Wastes, 5, 185 (1960).

this technique, approximately 25% of the original benzene was recovered. The losses were attributed to volatilization during concentration as evidenced by determination of a blank. Using this method, the total detectable organics in tap water were determined to be less than 0.2 ppm (equivalent to benzene) while none were detectable in the distilled water. However, organics at an original concentration in the range of 10 ppb can be determined using a 1000:1 concentration factor and an internal standard.

Porapak was found to give a better separation of both high and low boiling components than SE-30, the commonly used column material for organics. (D. G. Gillen)