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***Mound Laboratory Chemistry
and Physics Progress Report:
January-March 1970***

AEC Research and Development Report

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MOUND LABORATORY

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. ATOMIC ENERGY COMMISSION

PRINTED IN THE UNITED STATES OF AMERICA

Available from

Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

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Issued: October 23, 1970

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MONSANTO RESEARCH CORPORATION

A Subsidiary of Monsanto Company

MOUND LABORATORY

Miamisburg, Ohio 45342

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U.S. Government Contract No AT-33-1-GEN-53

Table of Contents

	<u>Page</u>
FOREWORD.	3
SUMMARY	4
SEPARATION CHEMISTRY	
Uranium-234 Recovery	7
Thorium-229 Recovery	9
ANALYTICAL CHEMISTRY	
Determination of Bismuth-210, Lead-210 and Polonium-210 by Liquid Scintillation Counting.	11
Determination of Niobium by 14-MeV Neutron Activation Analysis	12
Determination of Precision of Plutonium-238 Data on Various Recovery Solutions	16
Determination of Traces of Mercury in Oxygen-Free High- Conductivity Copper.	18
Evaluation of the Spectrophotometric Iron Procedure.	20
Interferences in Determining Selenium and Tellurium by Atomic Absorption	21
Precision in the 14-MeV Neutron Activation Analysis of Nitrogen	21
INSTRUMENTATION AND METHODS	
Improved Scanning for the Atlas CH-4B Mass Spectrometer.	24
REFERENCES.	25

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 W. T. Cave, Director, Nuclear Operations.

Previous reports in this series are:

MLM-1612	MLM-1531
MLM-1609	MLM-1526
MLM-1606	MLM-1520
MLM-1603	MLM-1494

Summary

SEPARATION CHEMISTRY

Uranium-234 Recovery Uranium batch U-6, recovered by extraction from waste raffinate solutions, was found to be grossly contaminated by natural uranium in the plutonium-238 recovery process. No further processing of this material at this low uranium-234 isotopic composition will be performed. Another batch (U-5) was found to contain 94.7% uranium-234. It has been processed through the final anion exchange step twice. Further purification will be required before it is converted to the oxide since it is contaminated with 300 ppm of plutonium-238 in 1.74 g of uranium-234.

Additional analytical data have been obtained to evaluate the new TOPO-APHA method of uranium-234 determination. The errors found for this method seem to be realistic, but could probably be reduced by further development work and by analyzing multiple samples.

A plutonium-zirconium alloy was allowed to spontaneously oxidize in air and then was dissolved in HNO_3 containing HF so that the uranium-234 could be eventually recovered. A fine, grey-colored material, believed to be zirconium oxide, precipitated when this solution was heated for a prolonged time. The resultant solution was processed by the standard homogeneous oxalate precipitation method. The zirconium which may have been present caused no problems in this part of the procedure, and only 0.4% of the starting plutonium remained in the supernatant solution. (Page 7)

Thorium-229 Recovery A new, semiautomatic apparatus for solvent extraction separation of thorium-229 from uranium-233 was assembled and tested. In the first run the aqueous fraction contained 2.7 mg of thorium-229 in 57 g of 11-yr-old uranium-233 in 2M HNO_3 . It was found that the organic recirculation rate was many times greater than the strip rate, causing depletion of the HNO_3 in the aqueous portion and transfer of appreciable amounts of thorium to the evaporator in the strip solution. The extraction was repeated using a lower organic recirculation rate of 3-5 ml/min, and 55% of the original 2.7 mg of thorium-229 was recovered. Most of the missing thorium was found to be in the evaporated uranium. (Page 9)

ANALYTICAL CHEMISTRY

Determination of Bismuth-210, Lead-210 and Polonium-210 by Liquid Scintillation Counting The principles of a method of determining bismuth-210, lead-210 and polonium-210 (RaD, E and F) in solution by liquid scintillation counting are presented. The method makes use of the three independent channels of pulse height analysis which are available. (Page 11)

Determination of Niobium by 14-MeV Neutron Activation Analysis The possibility of determining niobium by 14-MeV neutron activation analysis has been investigated. The reaction $^{93}\text{Nb}(n,2n)^{92}\text{Nb}$ with a 500-mb cross section appears to be the best approach. In this analysis, the 10.2-day activity of ^{92}Nb is detected by measuring its 0.934-MeV gamma radiation. (Page 12)

Determination of Precision of Plutonium-238 Data on Various Recovery Solutions To improve plutonium-238 precision (alpha mounting and counting) on various recovery solutions, the analysis precision is being compared to the sampling precision on 14 tanks in the recovery process areas. Preliminary data indicate that the greatest problem area for the recovery personnel is to obtain a representative sample in the recovery operations. (Page 16)

Determination of Traces of Mercury in Oxygen-Free High-Conductivity Copper A solvent extraction system was investigated along with spectrum stripping for the analysis of traces of mercury in copper by the standard additions method. The possibility of counting the samples with a Ge(Li) detector, without any chemical separation, was also investigated. The data points were scattered as in the previous procedure, so that the precision was very poor. These results indicate that it might be better to analyze several samples without any mercury being added to the original material. (Page 18)

Evaluation of the Spectrophotometric Iron Procedure Poor precision was attained recently when the standard spectrophotometric procedure was used for the analysis of iron in two plutonium nitrate samples. It was theorized that the o-phenanthroline complexing agent had been consumed by an impurity introduced by the sampling bottle's rubber septum. The procedure was modified to increase the quantity of complexing agent added, and more satisfactory results were obtained. (Page 20)

Interferences in Determining Selenium and Tellurium by Atomic Absorption Extremely low results (compared to the theoretical values) were obtained for selenium and tellurium when several rare earth selenides and tellurides were analyzed by atomic absorption using an argon-hydrogen flame. Use of the higher temperature acetylene-air flame eliminated the interference by the rare earths and other metal cations investigated. (Page 21)

Precision in the 14-MeV Neutron Activation Analysis of Nitrogen The overall relative standard deviation for the determination of nitrogen in the 0.1-0.8% range by 14-MeV neutron activation is approximately $\pm 10\%$. A multiple summation and spectrum smoothing are being investigated for increasing the precision. (Page 21)

INSTRUMENTATION AND METHODS

Improved Scanning for the Atlas CH-4B Mass Spectrometer A mass selector circuit was installed on an Atlas CH-4B mass spectrometer in order to decrease the time required for routine analysis of gaseous samples. An option allows the original mass selector circuit to be used for analyses not available on the selector switch. A scan reverse switch makes it possible to reverse the scan at any point. (Page 24)

Separation Chemistry

URANIUM-234 RECOVERY

The rare isotope of uranium of mass-234 is being recovered from two sources at Mound Laboratory. In the anion exchange process, used for the recovery and purification of plutonium-238 from scrap materials, uranium tends to be washed off the column, winding up in the waste anion exchange raffinate solution. Because of the large quantities of aged plutonium-238 materials processed in the scrap recovery system, this waste raffinate solution represents a rich source of uranium-234. The solvent extraction uranium-234 recovery facility and the process have been described previously.¹ A second source of uranium-234 is aged plutonium-238 materials at Mound Laboratory (i.e., "cows" held expressly for uranium-234 production, or aged heat source fuel material scheduled for reprocessing). Processing of these materials normally consists of dissolution and homogeneous oxalate precipitation in laboratory-scale equipment to separate the bulk of the plutonium, followed by evaporation of the uranium-containing supernatant solution.

Additional processing of the uranium product solution from either of the two sources consists of two cycles of anion exchange. An intermediate anion exchange step consists of loading uranium and plutonium onto an anion exchange column from an aluminum nitrate-salted medium, washing the uranium off with 7M HNO₃, and eluting the plutonium with dilute HNO₃.² The final anion exchange step also uses an aluminum nitrate-salted medium to load uranium (and the small amount of plutonium remaining) on the column, but then uses 9M HCl and a reducing agent (iodide ion) to reduce and wash off the remaining plutonium, before the uranium is eluted with dilute HCl.³

Uranium batch U-6, recovered by extraction from waste raffinate solutions, was taken through the intermediate anion exchange step. The product solution was analyzed and found to contain 0.97 g of uranium-234 and 0.6 mg of plutonium-238, indicating essentially complete recovery of the uranium while the plutonium contamination was reduced by a factor of 160. A sample of batch U-6 was submitted for mass isotopic analysis. The results listed in Table 1 indicate gross contamination by natural uranium somewhere in the plutonium-238 recovery process. Currently, there is no demand for uranium-234 at this low isotopic composition, and no further processing of this batch is planned.

Table 1

MASS ISOTOPIC ANALYSES OF URANIUM RECOVERY SAMPLES

<u>Mass</u>	<u>Isotopic Content (%)</u>	
	<u>U-5</u>	<u>U-6</u>
234	94.7	50.1
235	0.09	0.17
236	0.045	0.027
238	5.19	49.7

Mass analysis results on a sample of uranium batch U-5 (previously processed through the intermediate anion exchange step)² are also given in Table 1. The figure of 94.7% is close to the values found for previous batches of uranium-234 recovered from waste raffinate solutions, and indicates a modest contamination by natural uranium. This batch has been processed through the final anion exchange step twice. Analysis of the uranium-234 solution after the first processing showed 1.51 g of uranium-234 contaminated with 0.88 mg (580 ppm by weight) of plutonium-238. This solution was evaporated to dryness, taken up in dilute HNO₃, salted with aluminum nitrate, and the final anion exchange was performed again. Analyses after the second process showed 1.74 g of uranium-234 contaminated with 0.52 mg (300 ppm) of plutonium-238. This material will require additional purification before conversion to oxide.

Two batches of stored raffinate (totaling over 700 liters) were processed in the solvent extraction facility and the uranium products were designated U-8 and U-9. The extraction of U-9 was noteworthy in that it was necessary to add three times the normal amount of aluminum nitrate to obtain complete extraction of the plutonium. This behavior presumably was caused by the presence of above-normal amounts of fluoride ion.

Additional analytical data have been obtained to evaluate the accuracy of the new TOPO-APHA method of determining uranium-234 described in the last report.² These data are listed in Table 2. In both the TOPO-APHA method and the TOPO-PAN method,⁴ tri-n-octylphosphine oxide (TOPO) is used to purify the uranium, but the TOPO-APHA method uses alpha counting to determine the uranium-234 only, while the TOPO-PAN method uses a spectrophotometric measurement of a uranium complex to determine total uranium present. The assumed "true" uranium-234 values are the results of alpha counting after additional purification and, while subject to small errors, these values should be much better than any previous value. Total uranium values were calculated using the uranium-234 values and the isotopic ratios listed in Table 1. The errors found for the TOPO-APHA method seem to be realistic, but could probably be reduced by additional development work and by analyzing multiple samples. The error in U-5 by the TOPO-PAN method is much larger than it should be, and probably represents incomplete removal of interfering ions.

Table 2

COMPARISON OF URANIUM ANALYTICAL METHODS

<u>Analytical Method</u>	<u>Sample U-5</u>	<u>Error</u>	<u>Sample U-6</u>	<u>Error</u>
TOPO-APHA ^a	1.61 g U-234	+7%	0.82 g U-234	-15%
TOPO-PAN ^b	2.42 g U _{t.o.t}	+52%	2.18 g U _{t.o.t}	+12%
Found after purification ^c	1.51 g U-234 1.59 g U _{t.o.t}		0.97 g U-234 1.94 g U _{t.o.t}	

^aReference 5.^bReference 4.^cUranium-234 value by counting; U_{t.o.t} calculated using measured isotopic ratios.

One type of aged plutonium-238 heat source material presently available for uranium-234 recovery was originally in the form of a plutonium-zirconium metal alloy. The alloy was allowed to spontaneously oxidize in air, and the resulting oxide was dissolved in HNO₃, with HF added to accelerate the dissolution. It was observed that prolonged heating of these solutions resulted in the precipitation of an extremely fine, grey-colored material, believed to be zirconium oxide. One batch of this solution, designated A10-7, containing 10.6 g of plutonium, was processed by the standard homogeneous oxalate precipitation method.⁶ If any zirconium was present, it caused no problems in the procedure, and the amount of plutonium left in the supernatant solutions was quite low (an average of 33 mg/liter, or 0.4% of the starting plutonium). A second batch of solution, currently in process, seems to contain some zirconium and other impurities, some of which appear to precipitate with the plutonium, but further discussion will be deferred until additional data are available. (P. E. Figgins)

THORIUM-229 RECOVERY

A new, semi-automatic apparatus for laboratory-scale solvent extraction separation of uranium-233 and thorium-229 was assembled. The equipment consists of two magnetically stirred flasks, one for extraction and one for stripping, each a 250-ml erlenmeyer with an elongated neck and an overflow spigot near the top of the neck. Long-stem funnels deliver liquids entering the flasks directly to the stirring bars at the bottoms.

Approximately 150 ml of aqueous HNO₃ solution containing 40-80 g of uranium-233 is placed in the upper flask where it is continuously stirred with DSBPP-DEB (di-secondary-butyl phenyl phosphonate in diethyl benzene)

organic extractant which enters through the funnel from the top, then rises through the neck as it is loaded with uranium, and overflows through the funnel to the stirrer of the stripping flask. Strip solution ($0.005M$ HNO_3) is continuously metered to the stirrer through the same funnel. The organic phase, after stripping, rises in the neck, and overflows to an air lift pump which delivers it to the funnel at the top of the extraction flask to complete the circuit. The loaded strip solution flows down through a phase separation neck in the bottom of the stripping flask, over a weir to maintain the stripping flask liquid level, and into an evaporator-still where the uranium is recovered.

The apparatus is operated continuously until all of the uranium has been removed from the original aqueous solution. The contents of the extraction flask then are transferred to a separatory funnel where the aqueous phase is drawn off and extracted, single-stage, with TOPO (tri-n-octyl phosphine oxide) in DEB to recover the pure thorium. This, in turn, is stripped with oxalic acid solution, which is then evaporated to obtain the product thorium-229.

For the first run with the new apparatus, the aqueous fraction contained 59 g of 11-yr-old uranium-233, containing 2.7 mg of thorium-229, in $2M$ HNO_3 . The strip rate was set at 3 ml/min, the maximum which could be handled by the evaporator, while the air lift pump recirculated the organic at the rate of 20-30 ml/min. After the uranium was nearly all extracted, as determined by alpha analysis, the aqueous portion became cloudy and it was discovered that appreciable amounts of thorium were being transferred to the evaporator in the strip solution. It was found that the HNO_3 had been completely extracted from the aqueous portion, resulting in a nearly colloidal suspension of precipitated thorium. The suspension was progressing by mechanical transfer through the organic into the strip solution. The only difference between this run and previous runs with stirred separatory funnels was that, in this run, the organic recirculation rate was many times greater than the strip rate while previously it had been 1:1.

The aqueous phase was removed, evaporated to dryness, and fumed with concentrated HNO_3 to redissolve the thorium. The glass apparatus was rinsed with concentrated HNO_3 to remove the adsorbed thorium, which was added to the aqueous portion. The extraction apparatus was reassembled and the aqueous phase, now adjusted to $4M$ in HNO_3 , was re-extracted. An organic recirculation rate of 3-5 ml/min, approximately equal to the strip rate, was used. A total of 1.5 mg, or 55% of the original 2.7 mg, of thorium-229 was recovered. Most of the missing thorium-229 was found to be in the evaporated uranium and, presumably, will be recovered in the next "milking". The recovered thorium-229 is being held for consolidation with the next run.

A second batch, consisting of 60 g of uranium-233, from Cask #1 has been dissolved and will be extracted using the apparatus described above.
(M. R. Hertz)

Analytical Chemistry

DETERMINATION OF BISMUTH-210, LEAD-210 AND POLONIUM-210 BY LIQUID SCINTILLATION COUNTING

A method for determining bismuth-210, lead-210 and polonium-210 (RaD, E and F) in non-equilibrium (radioactive) solutions is required. The RaF can readily be measured by absolute alpha counting techniques, but beta counting by conventional methods is not valid where alpha emission is also present. A method for determination by liquid scintillation counting is being developed.

In the Packard Tri-Carb Liquid Scintillation Spectrometer, three independent channels of pulse height analysis are available. If we let:

A = dis/min of ^{210}Po (RaF; alpha emitter, $E = 5.30$ MeV)

B = dis/min of ^{210}Bi (RaE; beta emitter, $E_{\alpha, \alpha} = 1.17$ MeV and 0.060 MeV)

C = dis/min of ^{210}Pb (RaD; beta emitter, $E_{\alpha, \alpha} = 0.015$ MeV)

a_1, a_2, a_3 = efficiency for A in channels 1, 2, and 3 respectively

b_1, b_2, b_3 = efficiency for B in channels 1, 2, and 3 respectively

c_1, c_2, c_3 = efficiency for C in channels 1, 2, and 3 respectively

N_1, N_2, N_3 = counts/minute in channels 1, 2, and 3

It follows that:

$$N_1 = a_1 A + b_1 B + c_1 C \quad (1)$$

$$N_2 = a_2 A + b_2 B + c_2 C \quad (2)$$

$$N_3 = a_3 A + b_3 B + c_3 C \quad (3)$$

The constants in these equations can be determined in the following manner:

1. Set discriminator and gain on channel 1 so that $a_1 = 1.00$ and $c_1 > 0$, using ^{210}Po and ^3H standards.
2. Set channels 2 and 3 so that $c_2 = c_3 = 0$, $b_2 > 0$, and $b_3 > 0$, using ^{14}C , ^3H , and ^{26}Al standards.
3. Determine a_2 and a_3 , using a ^{210}Po standard.
4. Determine b_2 and b_3 using a calibrated equilibrium solution of RaD, E, F, so that $A = B = C = \text{a known value}$.
5. Using ^{26}Al (beta emitter, $E_{\text{max}} = 1.16 \text{ MeV}$) determine b_1/b_2 .
6. Determine c_1 from Equation 1, using the equilibrium solution.

Equations 1, 2 and 3 become:

$$N_1 = A + b_1 B + c_1 C \quad (4)$$

$$N_2 = a_2 A + b_2 B \quad (5)$$

$$N_3 = a_3 A + b_3 B \quad (6)$$

For a non-equilibrium solution, A, B and C can be determined from the above three equations. N_1 , N_2 and N_3 are observed values, and all the constants have been determined.

This method of determining RaD, E and F by liquid scintillation counting is presently being investigated. (M. L. Curtis and H. W. Kirby)

DETERMINATION OF NIOBIUM BY 14-MeV NEUTRON ACTIVATION ANALYSIS

Although little work has been done on the determination of niobium by 14-MeV neutron activation analysis, the work of Bramlitt and Fink⁷ suggests its feasibility. Table 3 gives data on the two reactions that might be applied to the neutron activation determination of niobium. The purpose of the present study was to determine whether analysis for niobium by 14-MeV neutron activation was possible, and to obtain some data on the sensitivity of the method.

A preliminary investigation consisted of irradiating two samples of niobium powder (Specpure Catalog No. JMC 601, ca. 99.7% pure) simultaneously with the Kaman Nuclear 14-MeV neutron generator using a neutron flux of $\sim 10^9 \text{ n/cm}^2/\text{sec}$. The samples, weighing 20.26 mg (No. 2) and 22.35 mg (No.3),

Table 3

NUCLEAR REACTIONS OF INTEREST IN THE
14-MeV NEUTRON ACTIVATION DETERMINATION OF NIOBIUM^a

<u>Reaction</u>	<u>Cross Section (mb)</u>	<u>Product Half-Life</u>	<u>Product Gamma Energies (MeV)</u>	<u>Abundances (%)</u>
$^{93}\text{Nb}(n,\alpha)^{90}\text{mY}$	6	3.1 hr	0.202 0.482	97 91
$^{93}\text{Nb}(n,2n)^{92}\text{mNb}$	500	10.16 day	0.934	99

^aReferences 7 and 8.

were mixed with pure powdered carbon and were heat sealed in 2-dram polyethylene vials. The single-axis rotator was used to ensure that each sample received an equal neutron flux. After a 10-min irradiation the samples were allowed to decay for 31 min and then counted several times over the next few weeks. The samples were counted simultaneously with two 2 x 2-in. (5.08 x 5.08-cm) NaI(Tl) well crystals used in conjunction with a RIDL 400-channel analyzer. The gamma spectrum of one of the samples after a 277-min decay is shown in Figure 1. The peaks correspond to the expected activities as indicated in Table 3. Since two different radiation detectors were used to measure the activities produced, a normalizing factor to correct the counts of one detector to the counts that would have been obtained on the other detector was required. This factor was determined by counting a ^{46}Sc source (emitting 0.89-MeV gammas) on both detectors--the right crystal and the left crystal. It was found that the counts obtained in the right crystal had to be multiplied by 1.03 to be compared with the counts in the left crystal. The deviation of this factor from 1.00 is believed to be almost entirely due to a difference in energy calibration between the two detector systems. Calibration with ^{46}Sc and ^{137}Cs standards indicated 10.0 keV/channel in the left crystal, and 9.62 keV/channel in the right crystal. Since an equal number of channels was used in obtaining the total photopeak count, then one would expect the above factor to be greater than 1.0. It was also observed that, although an energy shift occurred over the period of counting, this correction factor remained constant.

Net specific activities in counts per minute per milligram (cpm/mg) corrected for background, and corrected to counts that would have been obtained in the left crystal, are given in Table 4 for the 10.3-day half-life activity. These values were obtained from the total photopeak counts in a 1000-min count minus the background in the same energy region. Backgrounds were 7.49 cpm in the right crystal and 13.67 cpm in the left crystal. For a given count number the specific activities should agree since the samples were counted simultaneously and supposedly received the same

FIGURE 1 - Gamma spectrum of a niobium sample activated with 14-MeV neutrons, using a counting time of 100 min.

neutron flux. The data in Table 4, however, showed that the specific activity of sample No. 2 was always less than that of sample No. 3. Column seven in Table 4 gives the difference between the specific activity of sample No. 2 and that of sample No. 3.

Table 4

COUNTING DATA FOR 10.3-DAY ^{92m}Nb ACTIVITY

Count Number	Time (hr)	Sample No. 2 (Net cpm/mg)		Sample No. 3 (Net cpm/mg)		Difference (%)
		L ^a	R ^a	L ^a	R ^a	
4	36.34	1.38			1.51	8.7
5	106.8	1.13			1.25	10.2
6	133.6		1.083	1.12		3.3
7	150.9	0.998			1.10	8.9
8	179.9		0.954	0.984		3.1
10	225.1		0.832	0.879		5.3
11	275.4	0.699			0.783	10.7
12	325.0		0.618	0.655		5.7
13	372.6	0.553			0.605	8.6

^aL = Counts on the left crystal.

R = Counts on the right crystal.

All counts were corrected to counts on the left crystal.

These data then suggest a constant error of some type. Although a weighing error is possible, this is doubtful since a balance sensitive to about 0.05 mg was used. The error could be due to sample No. 3 receiving a slightly greater neutron flux than did sample No. 2. Further examination of these percentages indicates a grouping of the data into two sets: those cases where No. 2 is counted in the left crystal, and those cases where No. 3 is counted in the left crystal. In those cases where No. 2 is counted in the left crystal, the average difference is 9.4% ($\pm 1.0\%$, absolute standard deviation), whereas when No. 3 is counted in the left crystal the average difference is 4.3% ($\pm 1.3\%$). This difference between these two values suggests another constant error, which is apparently due to the use of two different detectors.

Because of these two apparent constant errors, the specific activity data of Table 4 were divided into four groups to evaluate the half-life of ^{92}Nb by the method of least squares. The half-lives and the 95% confidence intervals calculated by a linear regression analysis⁹ for the specific activities in columns 3, 4, 5 and 6 are 10.6 ± 0.6 , 9.8 ± 0.6 , 10.3 ± 1.0 , and 10.6 ± 0.2 days, respectively. The average half-life is 10.3 days, compared to the literature value of 10.16 days. The relatively good precision obtained in the determination of the half-life of ^{92}Nb is due to good counting precision, and indicates that good counting precision could be obtained in the determination of niobium by neutron activation analysis.

A study of the decay of the gamma peak at 0.48 MeV gave a half-life of 3.1 hr, in agreement with the literature value half-life for ^{90}Y . The gamma peak at 0.68 MeV (see Figure 1) is also believed to be due to ^{90}Y . It is probably the sum peak due to the 0.202-MeV and 0.482-MeV gammas of this isotope. It was observed, however, that the 0.48-MeV peak contained some other shorter-lived activity at 55 min after irradiation. This could have been due to ^{13}N , a positron emitter produced from irradiation of the nitrogen in the air that was not excluded when the sample was prepared.

In conclusion, it can be said that niobium can be determined by 14-MeV neutron activation utilizing the reaction $^{93}\text{Nb}(n,2n)^{92}\text{Nb}$. Sensitivity, however, is rather poor. For a sample containing 20 mg of niobium a relative standard deviation of about 5% would be expected. This assumes that there are no other long-lived activities, emitting gammas of energy greater than 0.75 MeV, produced in the irradiation of the matrix. If this were the case, corrections would have to be made in obtaining the counting rate of the 0.93-MeV photopeak.

Chemical separation of the interfering activities might be possible, but this would complicate the analysis. As far as the accuracy of the method, the two errors mentioned previously would have to be investigated further before any quantitative numbers could be given. Another disadvantage of the method, in addition to the poor sensitivity, is the fact that long counting times are required to attain good precision.

No further studies of this method will be undertaken.

(C. T. Bishop and E. B. Nunn)

DETERMINATION OF PRECISION OF PLUTONIUM-238 DATA ON VARIOUS RECOVERY SOLUTIONS

Difficulties have been experienced in obtaining satisfactory precision on various recovery solutions in the determination of plutonium-238 by alpha mounting and counting. To determine whether the problem was an analytical problem or a sampling problem, six samples were taken from a single tank and duplicate aliquots were taken from each sample for analysis. The data shown in Table 5 indicate that sampling was the major problem.

Table 5

COMPARISON OF ANALYTICAL RESULTS FOR PLUTONIUM-238 SAMPLES

<u>Sample Number</u>	<u>Analytical Dilution #1 (mg ²³⁸Pu/ml)</u>	<u>Analytical Dilution #2 (mg ²³⁸Pu/ml)</u>	<u>Deviation between Dilutions (%)</u>	<u>Maximum Deviation among Samples (%)</u>
1	0.573	0.570	0.53	39
2	0.462	0.444	4.1	
3	0.473	0.498	5.2	
4	0.421	0.423	0.48	
5	0.411	0.424	3.2	
6	0.525	0.520	0.96	

Further investigation was conducted with a tank from which six successive samples were taken. The data, shown in Table 6, showed that the plutonium-238 concentration generally decreased upon successive samplings. This indicated that solutions from previous sampling had evaporated in the sample line, and values could not approach the actual plutonium content until the line had been thoroughly rinsed with the new sample solution.

Table 6

SUCCESSIVE COMPARISON OF ANALYTICAL RESULTS FOR PLUTONIUM-238 SAMPLES

<u>Sample Number</u>	<u>Concentration (mg ²³⁸Pu/ml)</u>	<u>Deviation between Sample 1 & Sample 6 (%)</u>
1	11.25	22
2	9.67	
3	9.85	
4	9.68	
5	8.93	
6	9.23	

To resolve this problem, new sampling procedures were initiated in the recovery operations to ensure that sample contamination was not occurring during sampling. Also initiated was the sampling of 14 different recovery solutions, each five times, to determine where sampling problems (and possibly analytical problems) existed and what precision could be expected on a routine basis. To date, four of these solutions have been sampled, and the analytical data are shown in Table 7.

Again, the major portion of the precision problem still occurs with sampling. Investigations will continue with the remaining 10 tanks. If sampling continues to be the problem, other sampling methods will be investigated and/or more solutions will be taken for analysis to improve the statistics of the measurement. (M. J. Garrod, R. D. Terrell, C. R. Brown and W. R. Amos)

DETERMINATION OF TRACES OF MERCURY IN OXYGEN-FREE HIGH-CONDUCTIVITY COPPER

A method for the determination of trace quantities of mercury in oxygen-free high-conductivity (OFHC) copper by activation analysis is being investigated. It is hoped that mercury in the parts-per-billion concentration range may be determined with the high thermal neutron flux of the reactor at Wright-Patterson Air Force Base. Two grams of OFHC copper turnings with added mercuric nitrate standard (0.025 - 0.125 μg of mercury per gram of copper) were sealed in separate quartz vials and irradiated for 100 hr at a thermal neutron flux of about 5×10^{12} neutrons/cm²/sec. The mercury was added as a solution of mercuric nitrate and taken to dryness in a vacuum without heat. Two weeks were allowed for the decay of copper isotopes before radiochemical separations were performed.

An attempt to isolate the mercury by an anion exchange separation in a chloride system proved unsuccessful. Some mercury was lost by volatilization when the sample was heated to change from a nitrate system to a chloride system. When the nitrate was not removed and HCl was added to the solution for the first elution step, the mercury was not completely retained on the resin. Heating of the samples at any time should be eliminated.

Since some mercury was lost in the first elution in the ion exchange separation when high concentrations of nitrate were present, a solvent extraction separation of mercury from HNO₃ was investigated. Handley and Dean¹⁰ indicated that silver and mercury are selectively extracted from 6M or 9M HNO₃ with 30% tri-isooctyl thiophosphate (TOTP) in carbon tetrachloride. Extraction studies with 10 μg of mercury labeled with ²⁰³Hg tracer showed that mercury was quantitatively extracted in a single equilibration from 6M HNO₃ in the presence of a high concentration of copper. However, when the extraction efficiency was checked with a sample containing only 0.1 μg of mercury, the mercury was only 81.5% extracted.

Analysis of the organic phase from the extraction with TOTP was attempted with an NaI(Tl) detector. Since silver is also extracted and its Compton distribution contributes to the 0.279-MeV photopeak of ²⁰³Hg, a spectrum stripping technique was utilized to statistically remove the activity

Table 7

COMPARISON OF ANALYTICAL RESULTS OF VARIOUS PLUTONIUM-238 SAMPLES

<u>Sample Description</u>	<u>Sample Number</u>	<u>Analytical Dilution #1 (mg ²³⁸Pu/ml)</u>	<u>Maximum Deviation among Samples (%)</u>	<u>Analytical Dilution #2 (mg ²³⁸Pu/ml)</u>	<u>Maximum Deviation among Samples (%)</u>	<u>Deviation between Dilutions (%)</u>
Product (C-2 192)	1	7.98	5.8	8.20	6.3	2.8
	2	8.08		7.88		2.5
	3	8.32		8.32		-0-
	4	8.32		8.27		0.60
	5	8.45		8.38		0.84
Dissolver (D-3 285)	1	0.706	12	0.743	13	5.2
	2	0.702		0.715		1.9
	3	0.732		0.735		0.41
	4	0.782		0.773		1.1
	5	0.790		0.751		5.1
Fusion (D-1 307)	1	0.0134	10	0.0138	30	2.9
	2	0.0146		0.0120		22
	3	0.0136		0.0146		7.3
	4	0.0150		0.0128		17
	5	0.0140		0.0112		25
Ion Exchange Feed (C-4 ±E 124)	1	0.764	10	0.773	6.1	1.1
	2	0.825		0.795		3.7
	3	0.802		0.812		1.2
	4	0.842		0.812		3.6
	5	0.825		0.820		0.61

due to ^{110m}Ag and thereby yield a fairly well-defined photopeak for mercury. Four copper samples containing mercury for the standard additions method were analyzed using an NaI(Tl) detector with spectrum stripping. The organic phase in each case was also counted with a Ge(Li) detector. On the basis of these two analyses, the copper contained approximately 25 ppb mercury. However, the points were scattered so that the precision was very poor.

Another series of four samples for the standard additions method was counted in the quartz vials with a Ge(Li) detector without any chemical separation having been performed. The same scatter of data points resulted, indicating that there probably was some error in the addition of mercury, and that it might be better to analyze several samples without mercury being added.

The half-life of the 0.279-keV photopeak was followed over a period of 52 days. With four determinations in this period, a half-life of 51.0 days was observed, compared to the literature value of 46.9 days for ^{203}Hg .¹¹

Another batch of copper samples that contained no added mercury has been irradiated. The copper will be removed from the quartz vials for counting, but no chemical separations will be performed. Standards containing 0.025-0.100 μg of mercury were also prepared. The standards will be counted in the quartz vial because of the possibility of this small amount of mercury being absorbed into the quartz so that it cannot be quantitatively removed. (R. K. Gillette)

EVALUATION OF THE SPECTROPHOTOMETRIC IRON PROCEDURE

The spectrophotometric iron procedure used in the Plutonium Processing area was found to be inadequate in the case of two plutonium nitrate samples recently analyzed. Poor precision was attained, the data being biased on the low side. The problem was eventually traced to an insufficiency in the amount of iron-complexing agent added, which resulted in lowered iron results.

To investigate the problem, initially, the samples were run by standard additions. The results obtained by this technique confirmed that all of the iron was not being detected by the spectrophotometer. The iron present in the samples did not exceed the limits of the spectrophotometric procedure and, furthermore, sample history indicated no impurities different from those in other routine samples. However, the sampling bottle's rubber septum obviously had been attacked by the sample solution. It was theorized that the o-phenanthroline complexing agent was complexing an impurity introduced by the rubber septum.

To finalize the analysis investigation and establish the actual cause of the low results, three areas were examined. First, the reagent quality and instrument accuracy were checked and found to be within operating limits. Then, to check for proper iron reduction, the quantity of hydroxylamine hydrochloride was increased 2.5 times. No change was observed in the final

results. Finally, to ensure the presence of excess complexing agent, the o-phenanthroline was increased by a factor of five. The added complexing agent solved the problem.

The new procedure, with increased o-phenanthroline, was evaluated for analysis of solid solution material and found to be reliable up to certain limits. Up to 250 μg of iron can be determined in the presence of up to 90 mg of total plutonium and 10 mg of total thorium. These plutonium and thorium values were chosen to represent typical limits expected in the iron determination of solid solution material, although higher limits can exist. Satisfactory accuracy and precision were attained with this method. (D. C. Carter)

INTERFERENCES IN DETERMINING SELENIUM AND TELLURIUM BY ATOMIC ABSORPTION

Extremely low results were obtained for selenium and tellurium concentrations when several rare earth selenides and tellurides were analyzed by atomic absorption using an argon-hydrogen flame. This type of flame had been reported to improve considerably the sensitivity and detection limit for arsenic, selenium, tin and cadmium over the sensitivity utilizing the conventional acetylene-air flame.¹³ When the higher-temperature acetylene-air flame was used for analysis with the same standard and sample solutions as above, theoretical values for selenium and tellurium were obtained. Several metals representing each metal group of the periodic chart were checked for possible analytical interference in the atomic absorption determination of selenium using the argon-hydrogen and the acetylene-air flames.

Absorption measurements were made on solutions containing 100 $\mu\text{g}/\text{ml}$ of selenium and 100 $\mu\text{g}/\text{ml}$ of the metal under study in 1% HNO_3 , and then compared with a similar selenium solution containing no metal cations. The readings obtained using an acetylene-air flame and an argon-hydrogen flame are tabulated in Table 8.

Although the absorbance for the acetylene-air flame is approximately 40% of the absorbance in the argon-hydrogen flame, no interference is indicated by any of the metals tested. In the argon-hydrogen flame, of the cations investigated, only potassium, vanadium, copper and lead do not interfere.
(J. O. Frye)

PRECISION IN THE 14-MeV NEUTRON ACTIVATION ANALYSIS OF NITROGEN

Low levels of nitrogen (0.05 - 1.00%) are now being determined by a non-destructive 14-MeV neutron activation analysis procedure. The precision of this method is being investigated so that it can be incorporated into the general analytical procedure. A sample and a standard are irradiated, and then gamma-counted simultaneously. The area under the 0.511-MeV annihilation peak of the sample is compared to that of the standard and then corrected for a copper interference.

Table 8

METAL INTERFERENCES IN THE ATOMIC ABSORPTION
DETERMINATION OF SELENIUM WITH AN ARGON-HYDROGEN FLAME

<u>Cation Added to 100 μg/ml Selenium Solution</u>	<u>Absorbance in Acetylene-Air Flame</u>	<u>Absorbance in Argon-Hydrogen Flame</u>
None	0.29	0.77
Potassium	0.28	0.77
Calcium	0.28	0.46
Titanium	0.29	0.35
Vanadium	0.28	0.75
Chromium	0.28	0.52
Manganese	0.30	0.56
Iron	0.29	0.68
Cobalt	0.28	0.65
Nickel	0.28	0.57
Copper	0.28	0.77
Zinc	0.30	0.55
Aluminum	0.29	0.09
Lead	0.29	0.78

Past results were examined and the standard deviation was calculated for sets of duplicate analyses.¹⁴ The number of sets of samples, the range of nitrogen concentration, and the standard deviation are given in Table 9. The relative standard deviation is for the midpoint of the concentration range. Investigations are being made to determine why the absolute standard deviation increases with increasing nitrogen concentration.

Table 9

STANDARD DEVIATION FOR NITROGEN DETERMINATIONS

<u>Number of Duplicates</u>	<u>Nitrogen Concentration Range (%)</u>	<u>Absolute Standard Deviation (%)</u>	<u>Relative Standard Deviation (%)</u>
16	0.1 - 0.2	0.012	8.0
11	0.2 - 0.5	0.038	10.9
9	0.5 - 0.8	0.067	10.3

Two NaI(Tl) crystals, each adjusted to 10 keV/channel, were used for simultaneous counting of sample and standard. The area under the photopeak was determined by subtracting the baseline. The number of

channels, and therefore the energy range, was not necessarily the same for the sample and the standard. This could have been the source of some error.

The counting rate for the low-level nitrogen samples is low so that counting statistics are poor. The baseline correction is based on the number of counts in the boundary channels. When statistical variations are likely to be large, as with low count rate, the baseline correction is a likely source of error.

An equal number of channels for the sample and the standard are now being used so that the same energy range is studied. Several techniques are being investigated to see if the precision can be improved, especially when counting statistics are poor. A multiple summation¹⁵ and spectrum smoothing¹⁶ are being considered at this time. If these techniques appear useful, computer programs will be written for the calculations.
(R. K. Gillette and E. B. Nunn)

Instrumentation and Methods

IMPROVED SCANNING FOR THE ATLAS CH-4B MASS SPECTROMETER

A mass selector circuit was designed, built and installed on the Atlas CH-4B mass spectrometer in an effort to decrease the time required for routine analysis of a gaseous sample. With the original equipment it was necessary to select the mass peaks by rotating a ten-turn potentiometer in the magnet current regulator circuit until the peak was detected; then fine adjustment of the potentiometer was required until a position directly in front of the peak was obtained. The automatic scan circuit, in the magnet regulator, would then be used to scan the peak for analysis values.

With the new mass selector circuit, a 22-position rotary switch, with individual mass selector potentiometers, makes it possible to step to preselected masses and then scan each mass automatically. Switch positions for the masses that are normally detected in routine analysis were provided along with an option that allows the original mass selector circuit to be used for analyses not available on the selector switch. Incorporated also in this modification was a scan reverse switch which makes it possible to reverse the scan at any point by simply pressing a single-pole double-throw switch. When the scan reversing switch is released, the scanning circuit returns to the normal forward scan mode.
(J. R. Wetzell and D. L. Hobrock)

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