256
2/6/67

MLM-1342

MASTER

**MOUND LABORATORY QUARTERLY PROGRESS REPORT:
APRIL-JUNE, 1966**

J. F. Eichelberger, G. R. Grove and L. B. Gnagey

AEC Research and Development REPORT

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

MONSANTO RESEARCH CORPORATION

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

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

MIAMISBURG, OHIO

OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

U.S. GOVERNMENT CONTRACT NO. AT-33-1-GEN-53

Printed in USA. Price \$3.00. Available from the Clearinghouse for
Federal Scientific and Technical Information, National Bureau of
Standards, U. S. Department of Commerce, Springfield, Virginia.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights: or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

MLM-1342
TID-4500
Category - UC-2
Progress Reports

**MOUND LABORATORY QUARTERLY PROGRESS REPORT:
APRIL-JUNE, 1966**

J. F. Eichelberger
G. R. Grove
L. B. Gnagey

Date: June 30, 1966
Issued: Jan. 27, 1967

**RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS**

The Mound Laboratory Progress Report, issued quarterly, is intended to be a means of reporting items of current technical interest in research and development programs. To issue this report as soon as possible after the end of the quarter, editorial work is limited; and 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.

The previous reports in this series are:

MLM-1325	MLM-1274
MLM-1312	MLM-1268
MLM-1311	MLM-1266
MLM-1300	MLM-1254
MLM-1299	MLM-1250
MLM-1287	MLM-1245

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

MOUND LABORATORY

MIAMISBURG, OHIO OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

U.S. GOVERNMENT CONTRACT NO. AT-33-1-GEN-53

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

1

2

3

4

5

6

7

8

9

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	5
RADIOELEMENTS	
Half-Life Determination by Decaying Pairs	9
Separation and Half-Life Determination of Radon-219	11
Half-Life of Polonium-215	13
Levels in Radon-219 Populated by Alpha Decay of Radium-223	15
Valence Instability of Plutonium-238	19
Actinide Complexes	28
Hydrolysis of Uranyl Nitrate	28
Structure Studies	30
Thermal Dehydration of Uranyl Nitrate Hexahydrate	30
Thorium-229 Recovery	32
ANALYTICAL AND INSTRUMENTATION	
Nuclear Magnetic Resonance	38
Tritium Bremsstrahlung Counting	41
ORGANIC RESEARCH	
Adhesives Research	43

SUMMARY

RADIOELEMENTS

Half-Life Determination by Decaying Pairs After 230 days and 38 observations, the half-life of polonium-210 is found to be 138.528 ± 0.039 days by the decaying pair method, 138.329 ± 0.182 days by the variational method, and 138.316 ± 0.182 days by the general method.

Separation and Half-Life Determination of Radon-219 Radiochemical studies in the actinium-227 decay chain are reported. The half-life of radon-219 separated from its radium-223 parent was found to be 3.82 ± 0.05 sec. The gamma-ray spectrum of radon-219 is also reported, and the implications of the results are discussed.

Half-Life of Polonium-215 The half-life of polonium-215 was studied by observing polonium-215 decay events after the creation of the nuclide was indicated by the alpha decay of radon-219. The polonium-215 half-life is $(1.800 \pm 0.014) \times 10^{-3}$ sec.

Levels in Radon-219 Populated by Alpha Decay of Radium-223 Gamma ray spectra of radon-219 in coincidence with alpha groups from radium-223 were investigated. The photons were measured by gating on the four predominant alpha groups above α_{1270} . The results obtained are still considered preliminary.

Valence Instability of Plutonium-238 The experimental work on the valence instability of hexavalent plutonium-238 was essentially completed, but the lengthy and tedious calculations have not been completed yet. As the work approached completion, it became evident that the radiation mechanism suggested by the work might be further illuminated by studying the auto-reduction of hexavalent plutonium in dilute nitric acid at constant plutonium concentration in the presence of plutonium-238 at various concentrations. Therefore, determination of the rate of reduction of hexavalent plutonium in the presence of various proportions of the 238 isotope was undertaken. A solution containing 60% plutonium-238 reduced at an approximate rate of 7.6×10^{-3} mole/liter/hr, a solution containing 40% plutonium-238 at a rate of 3.4×10^{-3} mole/liter/hr, and a solution containing 20% plutonium-238 at a rate of 2.1×10^{-3} mole/liter/hr. These reduction rates were somewhat faster than anticipated, due, no doubt, to the large amount of catalyst added in order to decrease the time required to enter the zero-order region.

Actinide Complexes Investigation revealed that the triphenylphosphine oxide complex is formed when uranyl chloride reacts with triphenylphosphine because of air oxidation of the phosphine. When triethylphosphine or tri-n-propylphosphine is used, the corresponding diphosponium hexachlorouranate is formed. An analogous compound could not be prepared from thorium tetrachloride and triphenylphosphine.

Hydrolysis of Uranyl Nitrate The study of the hydrolysis of uranyl nitrate at constant metal concentration at 0°C was performed. The metal concentration studied ranged from 1.5×10^{-4} to $50 \times 10^{-4}M$, and the starting solutions were all 0.5N in nitric acid. Preliminary calculations based on the assumption that the (2,2), (1,1) species are in solution, yielded initial values of 2.3×10^{-7} and 2.9×10^{-8} . The dilution technique yielded values of 1×10^{-7} and 1.7×10^{-8} .

Structure Studies Single crystals of uranyl nitrate tri- and dihydrate were prepared, and the identities of the compounds were confirmed by analytical, x-ray powder diffraction, and infrared techniques. A single-crystal x-ray diffraction study was initiated on the dihydrate and the initial lattice parameters obtained agree with published values.

Thermal Dehydration of Uranyl Nitrate Hexahydrate The thermal dehydration of uranyl nitrate hexahydrate is being studied. Thermograms of uranyl nitrate tri- and dihydrate were obtained. No "phase change" for the dihydrate at 90°-95°C was observed in the present work, in contrast with the results reported in the literature.

Thorium-229 Recovery Dissolution of uranium tetrafluoride was demonstrated by two methods: (1) in a nitric acid-boric acid medium, and (2) in a water-aluminum nitrate mixture at temperatures of 100°C or less. The reaction was very smooth in both cases.

Separation of thorium from uranium was attempted on a cation exchange column at 80°C, an anion exchange column with mixed solvents (methanol-nitric acid), and an anion exchange column with nitric acid solutions of varying concentrations. The cation exchange column appears to give the best separation with no apparent loss of thorium to the uranium.

Screening tests of solvent extraction systems for the separation of trace concentrations of thorium-229 daughter from uranium-233 are underway. Initial screening tests have been run with three organic extractants in diethyl benzene (DEB) on a solution of uranium and thorium in 1M nitric acid. It appears that tri-n-octyl phosphine oxide (TOPO) extracts uranium first and then the thorium, but leaves thorium daughters in the aqueous phase. Tri-iso-octyl amine (TIOA) extracts thorium but leaves the uranium in the aqueous phase, whereas di (sec-butyl) phenyl phosphonate extracts uranium but leaves the thorium and its daughters.

ANALYTICAL AND INSTRUMENTATION

Nuclear Magnetic Resonance Methylstyrene undergoes hydrochlorination without polymerization when dry hydrogen chloride gas is bubbled through solutions of methylstyrene in n-heptane. The mode of reaction was revealed by analysis of the proton nuclear magnetic resonance spectra of the methylstyrene and the product of the reaction.

Tritium Bremsstrahlung Counting Studies were made on the effects of sample volume and entrance window characteristics on the bremsstrahlung counting rate of tritiated water. The highest sensitivity was obtained with a 5-mil beryllium window and a sample volume of 10 ml.

ORGANIC RESEARCH

Adhesives Research Boron trifluoride, BF_3 -PPEG (boron trifluoride-phenol-polyethylene glycol) and DB-VIII (zinc octanoate - triphenyl phosphite) were used with methyl nadic-hexachloroendomethylene tetrahydrophthalic anhydride mixtures in an effort to cure epoxy resins Epi Rez 5132, Epi Rez 502, CY 178 and CY 179 at room temperature. No satisfactory cures were obtained with the concentrations used. BF_3 -PPEG was also mixed with methyl nadic anhydride and with citraconic anhydride in catalytic amounts. The resultant mixtures were ineffective as room-temperature curing agents for epoxy resins Epon 812, Epon 828, Epon 871 and ERL 3794 at equivalent epoxy-anhydride molar concentrations.

Only small differences in specific resistivities were observed when hydroquinone was added in small concentrations (about 0.5 to 2%) to the silver-filled conductive adhesive formulation MC 1303-1. The pot life of the adhesive was drastically reduced by addition of the hydroquinone, and the gel time was reduced from about 85 to 35 min.

The shrinkage of Loctite adhesive 404, a cyanoacrylate adhesive, was determined by its change in weight in water during cure and by measurement of the density of the adhesive before and after cure. Shrinkage values of 15.7 and 15.1%, respectively, were obtained for the two methods. The curing time of the encapsulated adhesive was about 72 hr, probably due to the presence of volatile polymerization inhibitors.

1

2

3

4

5

6

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 radio-chemistry 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.

HALF-LIFE DETERMINATION BY DECAYING PAIRS

The half-life of polonium-210 (138.3763 ± 0.0017 days)¹ is being redetermined by alpha-counting, primarily to test the decaying pair method of computation² and to compare it with the variational and general methods³. The progress of the experiment during the first 143 days (27 observations) was summarized in a previous report⁴. After 230 days and 38 observations, the half-life of polonium-210 is found to 138.528 ± 0.039 days by the decaying pair method, 138.329 ± 0.182 days by the variational method, and 138.316 ± 0.182 days by the general method. Details of the analyses are given in Tables 1-4. (H. W. Kirby)

Table 1

HALF-LIFE OF POLONIUM-210 BY THE DECAYING PAIR METHOD
(38 Observations - 230 Days)

<u>Pair</u>	<u>Ratio</u>	<u>Half-Life (days)</u>	<u>Probable Error (days)</u>	<u>Absolute Error (days)</u>
1-2	0.618	138.542	± 0.130	+0.166
1-3	0.387	138.564	± 0.086	+0.188
1-4	0.261	138.530	± 0.069	+0.153
2-3	0.627	138.601	± 0.147	+0.225
2-4	0.422	138.517	± 0.081	+0.140
3-4	0.674	138.358	± 0.148	-0.018
Weighted Average		138.528	± 0.020 (Ext.) ± 0.039 (Int.)	+0.152

¹Mound Laboratory Progress Report for July, 1964, MLM-1209 (July 20, 1964) p. 12.

²Mound 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 (Jan. 28, 1966).

⁴Mound Laboratory Quarterly Progress Report: Jan.-March, 1966, MLM-1325 (March 31, 1966) p. 13.

Table 2

HALF-LIFE OF POLONIUM-210 AS COMPUTED BY THE
DECAYING PAIR AND GENERAL METHODS

n	Time Span (days)	By Decaying Pairs		By General	
		$T_{1/2} \pm \text{P.E.}$ (days)	Absolute Error (days)	$T_{1/2} \pm \text{P.E.}$ (days)	Absolute Error (days)
27	143	138.586 ± 0.074	+ 0.210	137.961 ± 0.519	- 0.415
28	157	138.610 ± 0.065	+ 0.234	137.832 ± 0.458	- 0.544
29	162	138.572 ± 0.061	+ 0.196	137.607 ± 0.350	- 0.770
30	168	138.570 ± 0.057	+ 0.194	137.672 ± 0.314	- 0.705
31	183	138.493 ± 0.055	+ 0.116	137.581 ± 0.276	- 0.796
32	190	138.493 ± 0.052	+ 0.117	137.674 ± 0.247	- 0.703
33	195	138.463 ± 0.049	+ 0.087	137.593 ± 0.223	- 0.784
34	202	138.507 ± 0.047	+ 0.131	137.767 ± 0.258	- 0.610
35	209	138.501 ± 0.045	+ 0.125	137.977 ± 0.220	- 0.399
36	212	138.521 ± 0.043	+ 0.144	138.051 ± 0.253	- 0.325
37	226	138.544 ± 0.041	+ 0.168	138.293 ± 0.194	- 0.084
38	230	138.528 ± 0.039	+ 0.152	138.316 ± 0.182	- 0.060

Table 3

HALF-LIFE OF POLONIUM-210 AND COUNTER RESOLUTION TIME
BY THE GENERAL METHOD
(38 Observations - 230 Days)

Sample	Half-Life (days)	Probable Error (days)	Absolute Error (days)	Resolution Time (min $\times 10^7$)
1	138.251	± 0.365	- 0.125	1.209 ± 0.277
2	139.093	± 0.327	+ 0.717	0.725 ± 0.153
3	137.824	± 0.299	- 0.552	1.189 ± 0.088
4	138.199	± 0.300	- 0.177	1.062 ± 0.060
Weighted				
Average	138.316	± 0.182 (Ext.) ± 0.160 (Int.)	- 0.060	1.070 ± 0.048 (Ext.) ± 0.046 (Int.)

Table 4

COUNTER RESOLUTION TIME BY THE KNOWN HALF-LIFE METHOD^a
(38 Observations - 230 Days)

<u>Sample</u>	<u>Resolution Time (min × 10⁷)</u>	<u>True Initial Counting Rate (cpm)</u>
1	1.115 ±0.040	151,268 ± 68
2	1.058 ±0.022	244,723 ±100
3	1.029 ±0.013	390,450 ±147
4	1.027 ±0.009	579,660 ±214
Weighted Average	1.0327 ±0.0065 (Ext.) ±0.0067 (Int.)	

^aBased on $T_{1/2} = 138.3763$ days

SEPARATION AND HALF-LIFE DETERMINATION OF RADON-219

The half-life and gamma-ray spectrum of radon-219 (actinon) was studied by separating radon-219 from its radium-223 parent in the apparatus shown in Figure 1. The radon-219 bulb was evacuated to a pressure of 0.1 torr, and the stopcock was turned to maintain the vacuum. The bulb was inserted in the well of a 3 × 3-in. NaI(Tl) detector, and the stopcock was opened so that the radon-219 accumulated in the radium-223 source portion would be drawn into the bulb. The stopcock was then closed to prevent diffusion of radon-219 into or out of the bulb, and the counting experiment was started.

The half-life of radon-219 was determined by feeding the output of the gamma-ray detector to a multichannel analyzer (MCA) operating as a multiscaler. Channel-advance signals were provided to the MCA from a time-base generator. Thus, the gross counting rate could be observed as a function of time. The time base selected for the radon-219 runs was 0.25 sec per channel, and the decay was followed for 200 channels, or 50 sec. The dead time between channels is set by the MCA, and is approximately 10 μsec. The experimental data were analyzed by a least-squares computer fit to the equation

$$Y = A + B^0 e^{-\lambda t}$$

where: Y is the count per channel at any channel number

A is the background count per channel

B^0 is the initial sample activity

t is the time elapsed since the beginning of the count

λ is the decay constant $[(\ln 2)/t_{1/2}]$

FIGURE 1 - Radon-219 Separation Apparatus.

The half-life of radon-219 was found to be 3.82 ± 0.05 sec, which is somewhat lower than the value recommended in 1931.⁵

The gamma-ray spectrum of radon-219 was also investigated by a technique similar to that discussed above for the half-life study. In this work, the MCA was operated in the pulse height analysis mode, and successive counts of radon-219 were made in the well crystal for 12-sec intervals. The gamma-ray spectrum is shown in Figure 2. Prominent gamma rays are observed at 270 and 406 kev, in good agreement with the data reported by Pilger.⁶ The decay scheme for actinon proposed by Pilger is shown in Figure 3; this scheme is supported by the present work. No cascade transition from the 404-kev level to the 272-kev state was observed, although a transition of 142 kev was postulated by Valli, et al.,⁷ from intensity-balance considerations.

The implication of the absence of the 142-kev transition is that the alpha decay of radon-219 to polonium-215 does not populate successive members of a rotational band in polonium-215. Since rotational bands based on a permanently deformed ground state are observed in the alpha decay of radium-223 to radon-219, this means that the onset of stable nuclear deformation probably occurs in the mass region 215-219. Further work, including high-resolution gamma-ray spectroscopy and alpha-gamma coincidence experiments, is in progress. (R. C. Lange)

⁵M. Curie, A. Debierne, A. S. Eve, H. Geiger, O. Hahn, S. C. Lind, St. Meyer, E. Rutherford and E. Schwindler, Revs. Modern Phys. **3**, 427 (1931).

⁶R. C. Pilger, Jr., Ph.D. Thesis, University of California Radiation Laboratory, Report UCRL-3877, July, 1957 (unpublished).

⁷K. Valli, J. Aaltonen, G. Graeffe and M. Nurmi, Ann. Acad. Sci. Fennicae: Ser. A, VI., **74**, 184 ('965).

FIGURE 2 - Gamma Spectrum of Radon-219.

HALF-LIFE OF POLONIUM-215

The half-life of polonium-215 has not been carefully studied since 1942, when Ward⁸ reported a value of $(1.83 \pm 0.04) \times 10^{-3}$ sec. The experimental technique used in the present work is similar to that used previously⁹ in

FIGURE 3 - Decay Scheme of Radon-219.

⁸A. G. Ward, Proc. Roy. Soc. (London), **181A**, 183 (1942).

⁹R. C. Lange, G. R. Hagee and J. T. McCarthy, J. Inorg. & Nuclear Chem., **28**, 651 (1966).

FIGURE 4 - Equipment Used in the Experimental Determination of the Half-Life of Polonium-215.

the determination of the half-life of the 0.305-Mev level in arsenic-75. A block diagram of the apparatus is shown in Figure 4.

A source of radium-223, in equilibrium with its daughter products, was placed in the detector chamber. A semiconductor surface barrier detector was used to observe alpha-decay events. A typical alpha spectrum from a radium-223 source is shown in Figure 5, where the alpha groups of the various members of the decay chain are identified. The amplified pulses

FIGURE 5 - Alpha Spectrum of Radium-223 and Daughters.

FIGURE 6 - Decay of Polonium-215, as Observed in Time-Base Experiment, after 4,751,356 Radon-219 Decay Events.

(Figure 4) are inspected by two single-channel analyzers (SCA) operating in parallel. The Gate SCA was set to provide a signal to the time-base generator (TBG) when an alpha particle from radon-219 was detected. This indicated that the nuclide polonium-215 had been created. The Signal SCA was set to provide a signal to the MCA when an alpha particle from polonium-215 was detected. The output of the Signal SCA was accepted by the MCA only when it had been turned on by the TBG. The TBG provided a series of channel-advance signals to the MCA, so that each channel represented a specific time interval. In this way, the decay of polonium-215 as a function of time could be observed.

The experimental results are shown in Figure 6, where the activity as a function of channel number (time) is plotted. These data were also analyzed by a least-squares computer fit to the equation $Y = A + B^0 e^{-\lambda t}$. The polonium-215 half-life was found to be $(1.800 \pm 0.014) \times 10^{-3}$ sec, in good agreement with the earlier report.⁸ (R. C. Lange)

LEVELS IN RADON-219 POPULATED BY ALPHA DECAY OF RADIUM-223

The level scheme of radon-219 as constructed by Pilger⁹ is shown in Figure 7. The transitions shown were placed by precise energy measurements of alpha groups and conversion electron lines. A few alpha-gamma coincidence studies were undertaken; however, the results were marginal due to the poor resolution of the NaI(Tl) gamma-ray detectors employed.

In view of the present availability of lithium-drifted germanium detectors it was deemed worthwhile to investigate the gamma-ray spectra and, in particular, the spectra in coincidence with alpha groups from radium-223. Because of the presence of the several short-half-life alpha-emitting lower members of this chain, the latter procedure is essentially the only practical means of selectively measuring photons from radium-223 decay. Therefore, experiments to measure photons by gating on pertinent alpha groups using the instrumentation described in the decay study¹⁰ of thorium-227 to radium-223 were begun.

¹⁰R. C. Lange, G. R. Hagee and J. T. McCarthy, Bull. Amer. Phys. Soc., Ser. II, 11, No. 3, 408 (1966).

FIGURE 7 - Decay Scheme of Ra^{223} as Derived by Pilger.
(Figure does not show 13 low-intensity alpha transitions to levels above 395 keV as reported by Walen, et al.¹¹)

Figures 8 and 9 show the results obtained in gating on the four predominant alpha groups above $\alpha_{127.0}$. The spectra from gating on α_{159} and α_{270} are interpreted as arising as Pilger has suggested in Figure 7. The placement of the 351 and 384-keV lines in the α_{338} spectrum are as yet uncertain. Presumably these arise from levels above 338 keV. The strong 270-keV line is partly the result of interference gating from α_{270} and possibly in part due to cascade feeding of the 270-keV level from 338 keV. This lower energy portion of the spectrum could not be seen in this measurement due to conditions in the biased amplifier.

¹¹R. Walen, et al., Nucl. Phys., 35, 232 (1962).

FIGURE 8 - Radium-223 Alpha-Gamma Coincidence Spectra; Energy Gates of Approximately 20 kev Centered on Alpha Groups Indicated (Peak Energies in kev).

FIGURE 9 - Radium-223 Alpha-Gamma Coincidence Spectrum;
Energy Gate of Approximately 20 kev on α_{448} (Peak Energies
in kev).

In Figure 9 the gamma rays at 445 and 449 kev are tentatively assigned to the feeding of the ground and low-lying state at 4.6 kev, whereas the 287-kev photon is interpreted as decay to the 159-kev level. A photon which appears at approximately 246 kev is tentatively thought to result from some interference gating from the alpha group feeding the 376-kev level with subsequent decay to the 127-kev level.

The above results are as yet considered preliminary. When all the ORTEC fast coincidence equipment is installed a more exacting series of experiments will be undertaken.

A cryostat assembly to house a lithium-drifted silicon detector at liquid nitrogen temperatures was placed in operation. It was found, however, that the detectors which were to be used in this assembly were failing when liquid nitrogen temperature was being reached. A newly designed version of these detectors which was supplied was found to be quite satisfactory, yielding a resolution of slightly less than 7 kev when cooled. The fault was attributed to a separation of contacts in the cooling process. This cryostat-silicon detector assembly is to be used in the measurement of gamma rays below 100 kev from the various nuclei under study. It will yield significantly better efficiency in this energy range than the germanium detector due to the depth of the dead layer in the latter. (G. R. Hagee).

VALENCE INSTABILITY OF PLUTONIUM-238

The experimental work on the valence instability of hexavalent plutonium-238 was essentially completed. As the work approached completion it became evident that the radiation mechanism suggested by the work might be further illuminated by studying the autoreduction of hexavalent plutonium in dilute HNO_3 at constant plutonium concentration in the presence of 60%, 40% and 20% plutonium-238. Determination of the rate of reduction of hexavalent plutonium in the presence of these proportions of the plutonium-238 isotope was thus undertaken.

The preparation of solutions of PuO_2^{+2} involved the use of divalent silver oxide and has been described elsewhere.¹² Surprisingly, unmolested solutions of pure plutonyl nitrate show considerable stability.

In agreement with Artyukhin, et al.,¹³ no reduction of the plutonyl cation in dilute HNO_3 is observed immediately after preparation, and it is possible to maintain $\text{Pu}^{238}\text{O}_2^{+2}$ solutions in dilute HNO_3 for as long as 2 weeks without the appearance of lower oxidation states of plutonium.

¹²G. L. Silver, "Determination of Plutonium in Dilute Nitric Acid by Complementary Tristimulus Colorimetry", Talanta (in press).

¹³P. I. Artyukhin, et al., Radiokhimiya, 1, 131-5 (1959).

One of the most revealing aspects of the reduction of solutions of $\text{Pu}^{238}\text{O}_2^{+2}$ is the observation that solutions of pure hexavalent plutonium are quite stable, but solutions which have been seeded with a small amount of plutonium in the trivalent and tetravalent oxidation states soon begin to reduce. This "valence wandering" is complete in a few days, depending upon the acidity. This observation, that the auto-reduction of the hexavalent state is apparently autocatalytic, was the first clue to the possible mechanism of the reduction reaction. Spectra of the reducing solutions, obtained periodically, were analyzed by computerized tristimulus colorimetry or the computerized quadrastimulus method. In the first case, the wavelengths used were those used in the equilibrium studies, and in the second case, the wavelengths were 475, 525, 560 and 600m μ . The coordinates w, x and y were used in ascertaining "q" values.

That the reduction of PuO_2^{+2} might be of an autocatalytic nature apparently did not occur to earlier workers interested in this problem, although an indirect suggestion of this mechanism can occasionally be found in earlier work. An excellent review by Connick of the oxidation-reduction reactions of plutonium contains a plot of the concentration of the trivalent, tetravalent and hexavalent species as a function of time.¹⁴ Apart from the time scale, which spans nearly two years, the graph in review describes with much similarity the valence wandering observed with plutonium-238 (Figure 10). Figure 11 illustrates this wandering in a somewhat different way, in the manner of a J_x - J_y plot commonly used in complementary tristimulus colorimetry. From these plots, it can be seen that the reduction of PuO_2^{+2} is accompanied by an increase in plutonium (IV) concentration, which reaches a maximum near the end of the reaction. This maximum is followed by a rather abrupt increase in plutonium (III) concentration. The graph in Connick's review describes the same phenomenon.

More recent, and perhaps more illuminating, is the interest expressed in the valence wandering phenomenon by Artyukhin.¹³ In a discussion of the subject, he remarks that "at first the reduction proceeds slowly, afterwards it increases". The reactions given by Artyukhin agree excellently with the autocatalytic model which is indicated by this work, but autocatalysis, per se, apparently did not occur to him. In agreement with Artyukhin, the apparent rate of reduction of PuO_2^{+2} is observed to decrease with increasing acidity.

If the reduction of the divalent plutonyl cation is autocatalytic, as seeding experiments might indicate, the rate of reaction (i.e., the rate of the disappearance of PuO_2^{+2}) should be related to the production of the concentrations of the hexavalent species and the autocatalytic agent¹⁵. It would at first appear that this would be either plutonium (III) or plutonium (IV). A plot of the variable terms in the integrated form of the proposed rate expression

¹⁴G. T. Seaborg and J. J. Katz, The Actinide Elements, New York, McGraw-Hill Book Co., 1954, Chapter 8.

$$\frac{-d\text{PuO}_2^{+2}}{dt} = k_1 (\text{PuO}_2^{+2})(\text{Pu}^{+3}) \quad (2)$$

$$\frac{1}{(\text{PuO}_2^{+2})_0 + (\text{Pu}^{+3})_0} \ln \frac{(\text{PuO}_2^{+2})_0 (\text{Pu}^{+3})}{(\text{Pu}^{+3})_0 (\text{PuO}_2^{+2})} = k_1 t$$

should give an s-shaped curve characteristic of autocatalysis.¹⁵ One such plot is shown in Figure 12, in which it has been assumed that the autocatalytic agent is the trivalent species. This figure is in agreement with that predicted if Pu^{+3} is the autocatalytic agent. That Pu^{+4} would not fit this model can be ascertained from the behavior of the logarithmic form of the integrated rate expression. The logarithmic term of this expression would not have the proper shape if the concentration of Pu^{+4} decreased near the end of the reaction as, in fact, has been observed.

FIGURE 10 - Autoreduction of Plutonium in 0.57M HNO_3 .

That Pu^{+4} is probably not the catalytic agent can be surmised on other grounds also. The tetravalent state could conceivably react with PuO_2^{+2} to yield two PuO_2^{+} ions; however, this reaction is unlikely to yield much PuO_2^{+} in view of the potential values of the III-IV and V-VI couples and the fact that such a reaction, involving the formation of plutonium-oxygen bonds, would probably be very slow. If it is assumed that the autocatalytic agent is Pu^{+3} , the mechanism of reduction is still not immediately apparent. But the fact that the trivalent species can reduce the hexavalent state, and that this reaction is fast, is well known.^{13, 16}

¹⁵A. A. Frost and G. R. Pearson, Kinetics and Mechanism, New York, John Wiley and Sons, 1953, Chapter 2.

¹⁶R. E. Connick, J. Am. Chem. Soc., **71**, 1528 (1949).

FIGURE 11 - J_x - J_y Plot for the Autocatalytic Reduction of Plutonium in 0.57M HNO_3 .

It would thus appear, as suggested by Artyukhin, that whatever species is involved, further reduction probably involves PuO_2^+ .

FIGURE 12 - Autocatalytic Reduction of PuO_2^{+2} .

It is not possible to ascertain the concentration of PuO_2^+ by the method of complementary tristimulus colorimetry as applied in this work. Also, since the concentration of PuO_2^+ in solutions of acidity much greater than $0.1M$ is never very large,¹⁷ poor mass balance or other obvious inconsistency in the spectrophotometric results is not necessarily to be expected. Examination of the spectra of reducing plutonium solutions by the method of computerized quadrastimulus colorimetry, however, lends support to the presence of plutonium (V). Examination of spectra by this method shows that the value of q_v is always very small (<0.02) and appears to vary as the product of the concentrations of the trivalent and hexavalent species. This would be expected if reaction 3 occurs.

Since it appears that Pu^{+3} is the more likely candidate to be involved in a reaction with PuO_2^{+2} , as indicated by Figure 12, it is of interest to ascertain the value of the specific reaction rate constant K_1 of

Equation 2. The product of the concentrations of plutonium species on the right side of the rate equation can be ascertained since the concentrations of PuO_2^{+2} and Pu^{+3} are known at various times after seeding from the spectra of the reducing PuO_2^{+2} solutions. The value of the derivative in this equation was obtained by plotting the concentration of PuO_2^{+2} as a function of time as shown in Figure 13. The lower portion of this typical plot can be roughly approximated by a straight line through the points in this region. This approximation is very rough since the concentration of PuO_2^{+2} is not a linear function of time, and such an approximation amounts to the statement that the reduction of PuO_2^{+2} during a small period of time is zero order.

¹⁷S. W. Rabideau and R. J. Kline, *J. Phys. Chem.*, **62**, 617 (1958).

FIGURE 13 - Plot of the Type Used to Determine $-d\text{PuO}_2^{+2}/dt$.

Evidently, however, this approximation is not wholly inaccurate in the acidity range examined, as can be seen from Table 5, which represents the absolute rate of reduction of PuO_2^{+2} ($-d\text{PuO}_2^{+2}/dt$) at various acidities. The rate of reduction of PuO_2^{+2} is approximately the same throughout the range of acidities shown in Table 5. Interestingly, the autoreduction of $\text{Pu}^{238}\text{O}_2^{+2}$ in 0.05M HCl and in 0.4M HNO_3 also seems to be approximately zero order.^{13, 14}

It is appropriate at this point to consider a question posed by examination of the plots in Connick's review and the report by Artyukhin: why is it, under similar conditions of acidity and distribution of the species Pu^{+3} , Pu^{+4} and PuO_2^{+2} , that $\text{Pu}^{238}\text{O}_2^{+2}$ reduces over a period of less than 200 hr, while $\text{Pu}^{239}\text{O}_2^{+2}$ is found to require about this number of days to effect the same reduction? Unfortunately, the reduction periods are not strictly comparable. The reduction described

by Connick employed millimolar plutonium, a concentration about one-tenth that employed in this study, and the process was also examined in hydrochloric acid. Nevertheless, if the reduction occurs exclusively by the sequence suggested by Equations 2 and 3, the rate of reduction of $\text{Pu}^{238}\text{O}_2^{+2}$ is faster than might be predicted by the behavior of $\text{Pu}^{239}\text{O}_2^{+2}$.

The autocatalysis model for the reduction of $\text{Pu}^{238}\text{O}_2^{+2}$ suggested by reactions 2 and 3 involves the rate-controlling step

The rate-controlling step is then presumably followed by such reactions as

generating more Pu^{+3} for use in reactions 3 and 4. Since the autoreduction of $\text{Pu}^{238}\text{O}_2^{+2}$ is truly a reduction process, it is in Equation 6 that the actual reduction step is postulated to occur, probably through interaction of Pu^{+4} with reducing agents generated by the effects of alpha radiations on the solvent.

The autocatalysis model has much to recommend it. It explains the necessary presence of lower oxidation states of plutonium, specifically Pu^{+3} , to initiate the reaction. It explains the relatively rapid increase of Pu^{+4} and the less rapid increase of Pu^{+3} . Near the end of the reduction, an abrupt increase in the concentration of Pu^{+3} occurs, and simultaneously an abrupt decrease in the concentration of Pu^{+4} also occurs. It is at this time that Pu^{+3} ceases to be consumed by reaction 4, and hence increases to its equilibrium value. It is also at this time that Pu^{+4} ceases to be generated by reaction 4, and hence decreases to its equilibrium value.

Table 5

RATES OF AUTOCATALYTIC REDUCTION OF HEXAVALENT PLUTONIUM-238

Acidity (M)	Pu (M)	$-\text{dPuO}_2^{+2}/\text{dt}$ (moles/liter-hr)	$(-\text{dPuO}_2^{+2}/\text{dt})/\text{Pu}$ (hr ⁻¹)
0.22	0.0122	3.7×10^{-4}	3.0×10^{-2}
0.25	0.0141	4.1×10^{-4}	2.9×10^{-2}
0.37	0.0136	4.3×10^{-4}	3.2×10^{-2}
0.37	0.0152	4.4×10^{-4}	2.9×10^{-2}
0.57	0.0121	3.4×10^{-4}	2.8×10^{-2}

Whatever the merits of the autocatalysis model, however, this mechanism is inadequate to explain the valence wandering of the plutonium-238 isotope. It cannot explain the apparent zero-order kinetics in the latter stages of the reduction. It cannot explain the higher rate of reduction of hexavalent plutonium-238 as compared to the similar reduction of hexavalent plutonium-239. The rate of reduction of the hexavalent state, using the prevailing concentrations of Pu^{+3} , cannot be made to fit the integrated form of Equation 2. The value of k_1 in this equation is not reproducible over the acidity range presented in Table 5. There is no improvement in the reproducibility of this constant if it is assumed that it is the concentration of PuO_2^{+2} , and not the concentration of PuO_2^{+2} , which belongs in Equation 2. Placing PuO_2^{+2} in Equation 2, and then substituting from Equation 3 into 2 yields:

$$-\frac{\text{dPuO}_2^{+2}}{\text{dt}} = \frac{k_1}{K} \frac{(\text{PuO}_2^{+2})(\text{Pu}^{+3})^2}{(\text{Pu}^{+4})} \quad (7)$$

which, again using the prevailing concentrations of the species Pu^{+4} , Pu^{+3} and PuO_2^{+2} , does not give reproducible values of k_1/K (where K is the equilibrium constant of Equation 3). Conversely, however, the reduction reaction is not zero-order throughout, because plots of the type shown in Figure 13 are not linear at high values of the concentration of the hexavalent species.

These considerations suggest that there may be two rate-controlling steps. Whichever step happens to be rate-controlling at a given instant depends upon the instant at which a reducing solution of $\text{Pu}^{238}\text{O}_2^{+2}$ is examined. The rate-controlling step at the start of the reaction allows the rate of reduction of the hexavalent species to increase, while the rate-controlling step near the end of the reaction causes this reduction to proceed at a nearly constant rate. This suggestion is enhanced by the observation that, with two restrictions, plots of the type shown in Figure 13 are nearly superimposable for all of the reductions described by Table 5. These restrictions are: it is necessary to shift the plots along the time axis in an arbitrary manner in order to obtain superimposability; and, however well other portions of the curves may overlap, the overlap at the top portion of the curve is poor.

Both of these restrictions can be explained by the autocatalysis model. The first can be explained by imagining differences in the amount of catalyst added, causing a linear shift along the time axis through the effect of this difference on the additive term

$$\frac{1}{(\text{Pu}^{+3})_0 + (\text{PuO}_2^{+2})_0} \ln \frac{(\text{PuO}_2^{+2})_0}{(\text{Pu}^{+3})_0}$$

in the integrated form of Equation 2.

The second restriction can also be explained by an autocatalysis model. The lower the acidity of the reduction reaction, the more rapidly the curves of the type shown in Figure 13 enter the zero-order region [i.e., the value of $d^2(\text{PuO}_2^{+2})/dt^2$ reaches a higher absolute value in solutions of low acidity than in solutions of higher acidity]. This is because the maximum permissible concentration of the catalytic agent, trivalent plutonium, is greater in solutions of low acidity than in solutions of higher acidity. Hence the initial rate of disappearance of PuO_2^{+2} changes more rapidly at low acidities.

It is difficult to propose a satisfactory explanation of the apparent zero-order kinetics which characterize the latter stages of the reduction of $\text{Pu}^{238}\text{O}_2^{+2}$. To explain this type of kinetics in these studies would do much to illuminate the valence wandering of plutonium-239, since the autoreduction of the hexavalent species of this isotope appears, at least according to the plots presented by Connick and Artyukhin, to be approximately zero-order throughout.^{13, 14}

Since Pu^{+3} is constantly being generated by the reduction of Pu^{+4} , the same reduction process should also be capable of reducing PuO_2^{+2} to PuO_2^{+} . Moreover, since the solutions are not at equilibrium and appear to be more reducing than similar solutions of the plutonium-239 isotope, the concentration of PuO_2^{+} in solutions of the plutonium-238 isotope is probably greater than that predicted by Equation 3. The zero-order region of the reaction is characterized by a reduction rate greater than that predicted by Equation 7. In 0.25M acid, the observed rate is about three times as fast as the rate predicted by Equation 7; in 0.57M acid the rate

is nearly thirty times as fast. If Equation 4 is to be preserved, the concentration of PuO_2^+ must, therefore, be larger than that predicted by Equation 3. The autoreduction experiments of hexavalent plutonium in 0.1M nitric acid as described by Artyukhin¹³ contain a concentration of PuO_2^+ which amounts to about 25% of the total plutonium present. Even accounting for the hydrolysis of Pu^{+4} , this is more than predicted by Equation 3. If the $\text{PuO}_2^{+2} - \text{PuO}_2^+$ reduction reaches equilibrium faster than Equation 3 reaches equilibrium, it is probably because the concentration of PuO_2^+ is potential-controlled; the reduction of PuO_2^{+2} to PuO_2^+ is thought to be rapid and reversible. The increased concentration of the pentavalent state over that predicted by Equation 3 allows an enhanced rate of reduction of PuO_2^{+2} according to Equation 4.

Zero-order kinetics implies that the rate-determining step near the end of the reduction reaction is the generation of PuO_2^+ . To reduce 0.01 mole of hexavalent plutonium requires 0.03 equivalent of reductant. Evidently the alpha radiations of the plutonium-238 isotope are numerous enough and energetic enough to produce this quantity of reductant in a few hours. This reduction must also act to keep the concentration of PuO_2^+ nearly constant, as this is a requirement of zero-order kinetics.

If the rate-determining step in the latter stages of the valence wandering reaction is the generation of pentavalent plutonium from hexavalent plutonium by radiation-related reducing agents, the rate of reduction of the hexavalent state should be dependent on the concentration of these reducing agents, and hence in some manner directly related to the concentration of the radioisotope. A higher concentration of plutonium-238 should be related to an increased rate of disappearance of PuO_2^{+2} . That there is such a dependence is illustrated by the last two columns of Table 5 which show the absolute rate of reduction of the divalent plutonyl ion ($-\text{dPuO}_2^{+2}/\text{dt}$) and the absolute rate of this reduction per mole of plutonium. These values appear to be independent of the acidity and show considerably less variation than the values of the absolute reduction rate given in the third column of Table 5.

It is suggested by this study that the increased rate of reduction of $\text{Pu}^{238}\text{O}_2^{+2}$ compared to the same rate for the plutonium-239 isotope is related to an increased concentration of pentavalent plutonium in solutions of the former. This difference can be related to the difference in the specific activity of these two isotopes. The rate of reduction of the hexavalent state is limited by: (a) limiting the concentration of catalytic agent (Pu^{+3}), in which case the reduction reaction appears to be autocatalytic, or (b) by limiting the quantity of pentavalent plutonium which, by virtue of the means by which the pentavalent state appears, causes the kinetics of the reaction to be zero order. For this reason the reduction of $\text{Pu}^{238}\text{O}_2^{+2}$ is at first autocatalytic, and later zero order. Perhaps it is for this same reason that the reduction of $\text{Pu}^{239}\text{O}_2^{+2}$ appears nearly zero order throughout. (G. L. Silver)

ACTINIDE COMPLEXES

Uranyl chloride and triphenylphosphine have been reported¹⁸ to form a yellow complex, $\text{UO}_2\text{Cl}_2 \cdot 2\text{R}_3\text{P}$ (where R = phenyl). However, a more recent report indicates that this complex does not exist,¹⁹ but that air oxidation of the phosphine results in the formation of the triphenylphosphine oxide complex, $\text{UO}_2\text{Cl}_2 \cdot 2\text{R}_3\text{PO}$. Work performed in our laboratory confirms that only the triphenylphosphine oxide complex is formed. The P=O stretching frequency in the nitrate and chloride complexes is observed in the infrared region at about 1070 cm^{-1} .

Allison and Mann have reported the formation of the molecular complex $(\text{R}_3\text{P})_2\text{UCl}_4$, where R = ethyl and n-propyl.²⁰ Gans and Smith have suggested that this complex does not exist but that the diphosphonium hexachlorouranate $[(\text{Ph}_3\text{PH})_2(\text{UCl}_6)]$ was formed.²¹ Our work indicates that only the diphosphonium complex is formed. The P-H stretch is observed at 2430 cm^{-1} for this compound.

An analogous compound could not be prepared from thorium tetrachloride and triphenylphosphine. (D. L. Plymale)

HYDROLYSIS OF URANYL NITRATE

The study of the hydrolysis of uranyl nitrate at 0°C was continued. Previous results²² were obtained by performing experiments at constant acidity (i.e., dilution experiments). In order to further evaluate the system the hydrolysis was studied at constant metal concentration.

The metal concentration studied ranged from approximately 1.5×10^{-4} to $50 \times 10^{-4} \text{ M}$. The starting solutions were all 0.05N in HNO_3 and all the titrations were performed with potassium hydroxide while a constant ionic strength of 0.1M was maintained.

In order to evaluate the data, a quantity $\bar{n}$ (the ligand number) is defined as

$$\bar{n} = \frac{C_{\text{OH}}}{C_{\text{M}}} \quad (8)$$

(i.e., $\bar{n}$ is the number of hydroxide ions n bound per metal ion).

¹⁸A. K. Majumdar, A. K. Mukherjee and R. G. Bhattacharya, J. Inorg. & Nuclear Chem., **26**, 386 (1964).

¹⁹B. W. Fitzsimmons, P. Gans, B. Hayton and B. C. Smith, J. Inorg. & Nuclear Chem., **28**, 915 (1966).

²⁰J. A. C. Allison and F. G. Mann, J. Chem. Soc., 2915 (1949).

²¹P. Gans and B. C. Smith, J. Chem. Soc., 4172 (1964).

²²Mound Laboratory Quarterly Progress Report: January-March, 1966, MLM-1325 (March 31, 1966) p. 33.

It is possible to calculate $\bar{n}$ from the experimental data using the equation

$$\bar{n} = \frac{B - C_H + [H^+]}{C_H} \quad (9)$$

where B = total concentration of base added

C_H = hydrogen ion concentration if no hydrolysis were taking place

$[H^+]$ = measured hydrogen ion concentration

The hydrogen ion concentration was evaluated from

$$E = E_0 + E_j - 59.16 \log [H^+] \quad (10)$$

and

$$pH = -\log \gamma [H^+] \quad (11)$$

where E_0 and E_j are the standard electrode potential and liquid junction potential, respectively, and γ is the activity coefficient. These constants were determined by preliminary acid-base titrations using the relationship $E_j = j [H^+]$ when j was found to be 9.5 mv/mole.

When $\bar{n}$ was plotted as a function of $\log [H^+]$ the complex formation curves shown in Figure 14 were obtained.

These curves indicate that polynuclear species are present, and that the species that are present are not formed by a "core-links" mechanism. Preliminary hand calculations, based on the assumption that the (2,2), (1,1) species are in solution, yielded initial values for the hydrolysis constants of 2.3×10^{-7} and 2.9×10^{-8} , respectively. The results obtained by the dilution technique yielded values of 1×10^{-7} and 1.7×10^{-8} . A computer program is being written in order to fully evaluate the experimental data. (W. Smith)

FIGURE 14 - Ligand Number as a Function of $\log [H^+]$.

STRUCTURE STUDIES

Single crystals of uranyl nitrate tri- and dihydrate were successfully prepared. The trihydrate was formed by cooling an acidic solution (35% HNO_3) of uranyl nitrate. The dihydrate was prepared by cooling, under vacuum, a 60% nitric acid solution of uranyl nitrate. The identities of these compounds were confirmed by analytical, x-ray powder diffraction, and infrared techniques.

A single-crystal x-ray diffraction study was initiated on uranyl nitrate dihydrate. The initial lattice parameters obtained ($a = 10.63 \text{ \AA}$, $b = 5.94 \text{ \AA}$ and $\beta = 72^\circ$) agree, within the limits of experimental error, with published values. The complete three-dimensional structure of this molecule, however, has not been reported, and data are being collected for the structure elucidation. (W. Smith, R. J. DeSando and P. W. Seabaugh)

THERMAL DEHYDRATION OF URANYL NITRATE HEXAHYDRATE

An investigation of the thermal dehydration of $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was initiated. It has been reported²³ that $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, when heated in a stream of air or in a stream of water vapor, melts at 65°C . In air the first four water molecules of water are supposedly lost at 110°C , leaving essentially the dihydrate at this point. At 175°C one more molecule of water is lost. The final dehydration to the anhydrous salt takes place between 210° and 220°C .

Figures 15 and 16 show several thermograms of uranyl nitrate tri- and dihydrate. Each peak in the thermograms has been successfully identified by x-ray powder diffraction techniques. It therefore appears likely that the thermal dehydration proceeds as follows:

Trihydrate:

Dihydrate:

One of the main differences observed in our results and the literature results is that no "phase change" has been observed in the present work for the dihydrate at 90° - 95°C . (W. Smith, R. J. DeSando and P. W. Seabaugh)

²³W. Lodding and L. Ojamaa, J. Inorg. & Nuclear Chem., **27**, 1261 (1965).

FIGURE 15 - Thermogram of Uranyl Nitrate Trihydrate.

FIGURE 16 - Thermogram of Uranyl Nitrate Dihydrate.

THORIUM-229 RECOVERY

Dissolution Various methods of dissolving UF_4 for recovery of thorium-229 from alpha decay of uranium were tested and several were found to give reasonable reaction rates. The resulting solutions containing large amounts of fluoride ion were very unstable as thorium fluoride precipitate forms in most solutions of HNO_3 and aluminum nitrate. Therefore, a suitable ion exchange feed solution requires nearly quantitative removal of fluoride ion prior to thorium-uranium separation.

One method of fluoride ion removal is oxidation of UF_4 to U_3O_8 according to the equation:

Superheated steam from a quartz heater is used to oxidize the uranium in an oxygen atmosphere in a platinum apparatus. This method is used for quantitative analyses of fluoride ion in UF_4 .

The products of the various dissolution tests were evaporated to dryness and calcined to UO_3 . The mixtures of UO_3 , H_3BO_3 , Al_2O_3 or ammonium diuranate were then calcined to U_3O_8 to remove the fluoride ion as HF , NH_4F , or traces of HF . Only 5 to 10 g were calcined at a time in a platinum crucible as considerable spattering of molten uranyl nitrate was observed.

The resulting oxides were analyzed for fluoride ion and the results are shown in Table 6.

Table 6

FLUORIDE CONTENT OF CALCINED UF_4

Sample Number	Oxide	Reagent Added in Dissolution	Temperature Final Oxidation ($^\circ C$)	Fluoride (%)
C-1	U_3O_8	$H_3BO_3 + HNO_3$	800	< 0.01
C-2	U_3O_8	NH_4OH (excess)	800	< 0.01
D-1	UO_3	$H_3BO_3 + NH_4OH$	600	0.11
D-2	UO_3	NH_4OH (excess)	800	0.11
D-3	U_3O_8	KOH	~100	0.14
D-4	U_3O_8	$(NH_4)_2C_2O_4 + NH_4OH$	800	9.60

The analytical results were obtained by titration of residual fluoride after distillation in a glass apparatus. It is not known what effect materials like boric acid have on the analyses. As analytical tests indicated that aluminum fluoride cannot be removed at 800°C from U_3O_8 , the analytical procedure may not be reliable with large amounts of AlF_3 and Al_2O_3 .

Dissolution of uranium tetrafluoride was demonstrated by two additional methods: (1) nitric acid with boric acid and (2) aluminum nitrate with water.

- (1) Five grams of uranium-233 tetrafluoride was dissolved in 25 ml of concentrated nitric acid by heating with 2 g of boric acid at 100°C for 4 to 6 hr, in accordance with the following equation:

The excess boric acid was removed by adding methanol and evaporating to dryness. The dissolution reaction was smooth and no problems were encountered.

- (2) Fifty grams of uranium tetrafluoride was dissolved and converted to uranyl nitrate by a reaction involving aluminum nitrate (100% excess) and water at a temperature between 85° and 95°C. The solution was evaporated to crystals, redissolved in water and evaporated to 100 ml. The reaction was smooth, except for an initial bit of foaming, but slow (8 to 10 hr). (W. S. Miller and W. S. Stringham)

Ion Exchange Studies The nitrate solution from the previous HNO_3 - H_3BO_3 dissolution was dissolved in about 50 ml of 8M HNO_3 and loaded into a 20-cm-long by 10-mm-diameter resin column of Dowex 1X8, 100 to 200 mesh. The feed was followed by 28 ml of 8M HNO_3 wash, 92 ml of 16M HNO_3 wash, and sufficient 0.5M HNO_3 until essentially all thorium was removed. The eluate was collected in 4-ml fractions for analysis. Alpha pulse analysis indicated a high loss of thorium through the column during feed addition. The uranium, however, eluted more rapidly than the thorium and the final elution with 0.5M HNO_3 contained a thorium product which was decontaminated from uranium by a factor of 1000.

The 100 ml of nitrate solution (pH = 1.5) from the aluminum nitrate dissolution was mixed with 900 ml of methanol for a feed solution for an anion exchange column. (A fine white precipitate, probably AlF_3 , formed when alcohol was mixed with the aqueous nitrate solution.) The feed was loaded on a 20-cm-long by 10-mm-diameter resin column of BioRad (Dowex) AG1X8, 100 to 200 mesh, and eluted at about 0.5 ml/min. The feed was followed by a 90% methanol - 10% 5N HNO_3 wash. The white precipitate passed through the column with only a slight holdup. Figure 17 shows the elution pattern for uranium, aluminum and fluoride by weight, and thorium-234 by gamma count of the 63-kev gamma peak. The thorium loss during the feed eluate may be associated with the precipitate of AlF_3 passing through the column.

FIGURE 17 - Separation of Thorium-234 from Uranium-238 in Mixed Solvents on a Dowex Anion Column.

Auranyl chloride solution (6×10^7 dpm uranium-232, -233 in 20 ml of 2M HCl) was loaded on a cation resin column (BioRad AG 50W-X8, 50 to 100 mesh) 6 mm in diameter and 50 cm long, heated to 80°C. The column was then washed with 2M HCl, 2M HNO₃, 4M HNO₃, and water. The thorium was eluted with 0.5M ammonium acetate at a pH of 3.85. Figure 18 shows the elution pattern for uranium and thorium as determined by alpha pulse analysis using the uranium-233 and thorium-228 alpha energy peaks. No thorium-228 could be detected before the ammonium acetate elution. (W. S. Stringham and D. H. Swanson)

Solvent-Extraction Studies Screening tests of solvent extraction systems are underway. Initial tests involve hand-shaken separatory funnels; the tests are being run on spiked solutions and evaluation of the results is by gross alpha counting.

Tests to date have been run on a synthetic aqueous solution containing 25 g/liter of natural uranium and 12.5 mg/liter of thorium in 1M HNO₃. For each organic extractant two parallel tests were run in which the uranium-thorium solution was spiked with either thorium-230 or uranium-233.

The three organic solutions tested to date are: 0.1M tri-n-octyl phosphine oxide (TOPO), 10 vol % tri-iso-octylamine (TIOA), and di(sec-butyl) phenyl phosphonate (DSBPP), each in diethyl benzene (DEB) diluent. Each run was made by sequential extraction of 20 ml of the uranium-thorium solution with three 20-ml portions of the organic. Ten-lambda quantities for alpha slides were taken from the initial solutions and from both phases after each extraction. Since the organic and aqueous solutions were of equal volume and all slides were prepared from 10 lambda of solution, the raw alpha counts were a direct measure of the results. In cases where the uranium was extracted a rough check on the progress could be made by observing the transfer of the yellow color. The results are given in Table 7.

The results can be summarized as follows: TOPO extracts uranium first, after which thorium is extracted. TIOA extracts thorium without extracting appreciable uranium, even though the thorium is present in only milligram quantities. DSBPP extracts the uranium without extracting appreciable thorium.

From the initial tests it appears that DSBPP might be used for the uranium-thorium separation, TIOA for concentration of thorium from intermediate solutions, and TOPO for scavenging thorium from dilute purified solutions.

Future work will include use of different acidities of the aqueous solutions, different acid ions, stripping tests, separation by selective stripping from the organic, and tests on uranium-233 solutions which might be produced from current methods of UF₄ dissolution. (M. R. Hertz)

FIGURE 18 - Separation of Uranium from Thorium on BioRad Cation Resin AG 50W-X8 (50 to 100 mesh) at 80°C by Alpha Pulse Analysis.

Table 7

COUNTS PER MINUTE PER TEN LAMBDA FROM
SOLVENT EXTRACTION SEPARATION

0.1M Tri-n-octylphosphine Oxide (TOPO)

	Thorium Spike		Uranium Spike	
	<u>Aqueous</u>	<u>Organic</u>	<u>Aqueous</u>	<u>Organic</u>
Before Spike ^a	189	-	201	-
After Spike	<u>928</u>	-	<u>947</u>	-
	739 ^b		817 ^c	
First Extraction	782	110	543	293
Second Extraction	605	242	292	505
Third Extraction	10	<u>506</u>	149	<u>117</u>
		858		915

10 Vol % Tri-iso-octylamine (TIOA)

	Thorium Spike		Uranium Spike	
	<u>Aqueous</u>	<u>Organic</u>	<u>Aqueous</u>	<u>Organic</u>
Before Spike ^a	190	-	216	-
After Spike	<u>920</u>	-	<u>912</u>	-
	730 ^b		782 ^c	
First Extraction	435	331	786	136
Second Extraction	258	136	724	110
Third Extraction	188	<u>44</u>	601	<u>58</u>
		511		304

10 Vol % Di(sec-butyl) Phenyl Phosphonate (DSBPP)

	Thorium Spike		Uranium Spike	
	<u>Aqueous</u>	<u>Organic</u>	<u>Aqueous</u>	<u>Organic</u>
Before Spike ^a	195	-	198	-
After Spike	<u>950</u>	-	<u>961</u>	-
	755 ^b		831 ^c	
First Extraction	748	89	488	280
Second Extraction	793	46	280	139
Third Extraction	773	<u>21</u>	211	<u>47</u>
		156		589

^a All counts before spike assumed due to uranium

^b Counts due to thorium-230 tracer

^c Counts due to natural uranium + uranium-233. Uranium-233 daughters have been subtracted out at 130 cpm per 10 lambda.

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.

NUCLEAR MAGNETIC RESONANCE

Hydrochlorination of Methylstyrene Prepolymer The purpose of this investigation was to determine whether methylstyrene monomer reacts with HCl and, if it does, where the reaction takes place. The reaction product of dry HCl gas with methylstyrene in n-heptane was analyzed by nuclear magnetic resonance (NMR) to determine the nature of the reaction.

Hydrogen chloride attacks the vinyl group of methylstyrene with addition of the chlorine atom to the carbon atom bonded directly to the benzene ring and the hydrogen atom to the terminal CH₂ group.

The proof for this mode of reaction is revealed in the proton NMR spectra of p-methylstyrene (Figure 19) and of the reacted methylstyrene (Figure 20). The spectrum of methylstyrene consists of five sets of peaks: four quartets and a singlet, ascribed, in the order of increasing magnetic field, to the four hydrogen atoms of the benzene ring, the H₂, H₃, and H₄ atoms of the vinyl group, and finally the p-methyl group on the ring. The spectrum dramatically changes to that of Figure 20 in which the addition of HCl to methylstyrene simplifies the spectrum to two quartets, a singlet, and a doublet. The smaller quartet is due to the resonance of the CH hydrogen atom associated with the chlorine and the doublet is due to the terminal methyl group. The quartet of the benzene hydrogen atoms and the singlet of the p-methyl group remain unaltered. The ratio of the areas of each set of peaks follows in the same ratio as the number of hydrogen atoms ascribed to each set of peaks, namely, 4:1:1:1:3 in methylstyrene and 4:1:3:3 in hydrochlorinated methylstyrene. (A. Attalla and R. R. Eckstein)

FIGURE 19 - Proton NMR Spectrum of p-Methylstyrene.

FIGURE 20 - Proton NMR Spectrum of Hydrochlorinated p-Methylstyrene.

TRITIUM BREMSSTRAHLUNG COUNTING

Bremsstrahlung counting with sodium iodide crystals is used extensively at Mound Laboratory to measure tritium in samples which cannot be assayed by other means without elaborate sample preparation. In an effort to increase the sensitivity of the method, studies were made of the effects of sample volume and entrance window characteristics on the bremsstrahlung counting rate of tritiated water.

Standardized tritiated water in 1 to 10-ml aliquots was introduced into circular 3-mil polyethylene bags by means of a hypodermic syringe. These samples were counted first with a 2-mm-thick, 3-in.-diameter sodium iodide crystal with a 1-mil aluminum entrance window, and then with a crystal of the same size with a 5-mil beryllium window. The relative counting rates are plotted as a function of sample volume for each type of window (Figure 21). Since the amount of radiation in the range of 0-20 kev transmitted through 5-mil beryllium is greater than that transmitted through 1-mil aluminum, the counting rate is higher with beryllium windows. It continues to increase as sample is added, to a total volume of 10-ml and higher, with either type of window. The greatest difference in transmission through beryllium and aluminum is at the very low end of the spectrum.²⁴ Hence, the peak occurs at a higher energy through the aluminum window, since much of the softer radiation which is absorbed by the aluminum is able to penetrate the beryllium. This is shown in Figure 22.

The crystals are coupled to phototubes selected for low noise. As a result, the background in the tritium energy range is about 10 cpm. The lower limits which can be measured by this technique, with counts equal to the background or higher, were computed and are listed in Table 8. (M. L. Curtis)

Table 8

SENSITIVITY OF TRITIUM BREMSSTRAHLUNG COUNTING

<u>Window</u>	<u>Sample Volume (ml)</u>	<u>Lower Limit Detectable (μc/ml)</u>
5-mil Be	2	1.4
5-mil Be	10	0.7
1-mil Al	2	2.3
1-mil Al	10	1.1

²⁴C. E. Crouthamel, "Applied Gamma-Ray Spectrometry", International Series of Monographs on Analytical Chemistry, Vol. 2, New York, MacMillan Company, 1960, p. 3.

FIGURE 21 - Effect of Sample Volume and Crystal Entrance Window on the Bremsstrahlung Counting Rate.

FIGURE 22 - Tritium Bremsstrahlung Spectra.

ORGANIC RESEARCH

In support of other programs at Mound Laboratory, research is being conducted on filled plastics, foams and adhesives for specialized applications.

ADHESIVES RESEARCH

Boron trifluoride, a boron trifluoride-phenol-polyethylene glycol mixture (BF_3 -PPEG, Allied Chemical Corp.), and a zinc octanoate-triphenyl phosphite mixture (DB-VIII, Argus Chemical Corp.) were added as accelerators to 40:60 methyl nadic anhydride-hexachloroendomethylene tetrahydrophthalic anhydride mixtures in an effort to cure various epoxy resins at room temperature. The epoxy resins investigated (Epi Rez 5132, Epi Rez 502, CY 178 and CY 179) were blended with the accelerator-anhydride mixtures in a 1:1 epoxy-anhydride molar ratio. No suitable cured systems were obtained with any combinations. BF_3 -PPEG was also blended with methyl nadic, citraconic, and dodecenyl succinic anhydrides in a weight ratio of 1 part of accelerator per 100 parts of anhydride. The accelerated anhydrides were then mixed with epoxy resin Epon 812, Epon 828, Epon 871 and ERL 3794 in a molar ratio of 1 epoxy to 1 anhydride. No room-temperature curing was observed.

Hydroquinone was recently reported to lower the specific resistivity of a silver-filled conductive adhesive formulation when substituted weight for weight for a small portion (2%) of the silver.²⁵ Accordingly, various amounts of hydroquinone (about 0.5 to 2%) were substituted for silver flake in the production adhesive MC 1303-1 formulation. The variations were used to glue conductivity test plugs in the usual manner; the test assemblies were allowed to stand at room temperature overnight, then post cure at 70°C for 1 hr. After standing 5 hr longer at room temperature, specific resistivities of the assemblies were measured; the results are shown in Table 9. Apparently lower specific resistivities were obtained when hydroquinone was incorporated into the production adhesive formulation, but the difference was very slight. Hydroquinone

²⁵B. Miller, "Polymerization Behavior of Silver-Filled Epoxy Resins by Resistivity Measurements", J. Appl. Polymer Sci., 10, 217 (1966).

is relatively insoluble in the epoxy resin; it forms a suspension rather than a true solution. The pot life of the adhesive was drastically reduced by hydroquinone addition. Gel time was reduced from 83-87 min (control) to 32-35 min for the formulation containing about 2% hydroquinone. The gel time was taken as the time elapsed between the addition of the hardener to the appearance of the first gelled particles.

The effects of the addition of hydroquinone, benzoquinone and 2,6-dichlorobenzoquinone on the gel times of a Hysol 2038 - Hysol 3471 (10:3 and 10:2.5) adhesive formulation were also determined. The additives were dissolved by heating in Hysol 2038, then cooled and mixed with Hysol 3471. All three additives reduced the gel times (Tables 10 and 11).

The cure shrinkage of Loctite adhesive 404 (Loctite Corporation), a cyanoacrylate type adhesive identical with Eastman 910 was determined by the buoyancy method developed earlier.²⁶ The adhesive was carefully poured into a contractable cylinder (the finger of a rubber latex glove) which had previously been moistened with water. The open end was quickly sealed by applying pressure to the thin film of resin adhering to the inside wall. The change in weight of the container in water was determined by means of the Instron testing machine in the usual manner. Figure 22 is a plot of weight change as a function of time for one of the two runs made. An inhibition period of about 18 hr was shown in each run; this inhibition is probably due to the presence of volatile additives which must be effectively neutralized before the curing process can accelerate. After this period curing proceeded somewhat faster. The total curing time was about 72 hr.

The shrinkage was calculated (a) from the change in weight of the encapsulated resin, and (b) by the difference in density of the resin before and after cure.

(a) Total weight of encapsulated resin = 14.864 g

Original weight in water = 1.38 g

Final weight in water = 3.47 g

Original weight in air - original weight in water = 13.48 g

Original weight in air - final weight in water = 11.39 g

Original density = 1.102 g/cc

Final density = 1.305 g/cc

²⁶R. A. Fischbein, J. Sci. Instr., 43, No. 7, 480 (1966).

$$\text{Shrinkage} = \frac{1.305 - 1.102}{1.305} = 15.7\%$$

(b) Original density of resin (by pycnometer) = 1.098 g/cc

Final density of resin (by displacement) = 1.293 g/cc

$$\text{Shrinkage} = \frac{1.293 - 1.098}{1.293} = 15.1\%$$

Agreement between the two methods was very good. (E. G. Thomas, R. Ratcliffe and J. V. Dichiaro)

FIGURE 23 - Change in Weight of Loctite Adhesive 404 During Cure.

Table 9

EFFECT OF HYDROQUINONE ADDITION ON THE SPECIFIC RESISTIVITY
OF CONDUCTIVE ADHESIVE FORMULATIONS

Formulation No.	Material (g)				Number of Resistivity Plugs	Resitivity (ohm-cm)		
	MD-750 Silver Flake	Hysol 2038 Epoxy Resin	Hysol 3471 Hardener	Hydro- quinone		High for Single Plug	Lowest for Single Plug	Average for All Plugs
1 ^a	18	10	3	None	8	0.022	0.017	0.019
2	17.92	10	3	0.08	8	0.018	0.013	0.015
3	17.84	10	3	0.16	8	0.014	0.011	0.012
4	17.69	10	3	0.31	8	0.016	0.013	0.014
5	17.38	10	3	0.62	10	0.016	0.013	0.014

^aProduction adhesive formulation MC 1303-1.

Table 10

EFFECT OF HYDROQUINONE ON THE GEL TIME OF
HYSOL 2038 - HYSOL 3471 ADHESIVE FORMULATION (10:3)

<u>Formulation No.</u>	<u>Hydroquinone (g)</u>	<u>Onset of Gelation (min)</u>	<u>Remarks</u>
1	None	64-67	Hysol 2038 not heated before mixing with the hardener.
2	None	55-58	Hysol 2038 heated and allowed to cool to room temperature before using.
3	0.08	36-38	In formulations 3 through 6, the hydroquinone was dissolved in the Hysol 2038 by heating. The solutions were allowed to cool to room temperature before mixing with the hardener.
4	0.16	28-30	
5	0.31	19-21	
6	0.62	11-12	

Table 11

EFFECT OF HYDROQUINONE, BENZOQUINONE, AND 2,6-DICHLOROBENZOQUINONE
ON THE GEL TIME OF HYSOL 2038 - HYSOL 3471 ADHESIVE FORMULATIONS

<u>Formulation No.^a</u>	<u>Material (g)</u>					<u>Onset of Gelation (min)</u>
	<u>Hysol 2038 Epoxy Resin</u>	<u>Hysol 3471 Hardener</u>	<u>Hydroquinone</u>	<u>2,6-Dichloro- benzoquinone</u>	<u>Quinone</u>	
1	10	8	0.16	-	-	33-35
2	10	2.5	0.16	-	-	40-44
3	10	3	-	0.25	-	21-24
4	10	2.5	-	0.25	-	42-45
5	10	3	-	-	0.16	33-36
6	10	2.5	-	-	0.16	38-41

^aIn all formulations, the quinone, hydroquinone, or 2,6-dichlorobenzoquinone were dissolved in the Hysol 2038 by heating and the resulting solutions were allowed to cool to room temperature before mixing with Hysol 3471.