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SUMMARY

RADIOELEMENTS RESEARCH

Uranium-234 Separation and Purification Mound Laboratory is separating and purifying uranium-234 from aged plutonium-238 solutions by a combination of anion exchange and solvent extraction techniques. A sample containing 2 g of uranium-234 is now being processed through the anion exchange step. In the latest ion exchange run 87% of the uranium was separated from 93% of the plutonium. Cold work on the purification of uranium by anion exchange from a high nitrate salt, low nitric acid medium continued. In eight runs an average 99.7% copper and 98.6% iron were removed from solution. A solvent extraction procedure also being investigated for purifying uranium gave an average 97.3% recovery.

Polonium The optical absorption spectra of the complex ions PoCl_6^- , PoBr_6^- , and PoI_6^- were obtained. The colors of the anion complexes were due to charge-transfer absorptions in which electrons in metal orbitals were excited to orbitals localized mainly on the ligands. Tentative decay schemes for polonium-208 and polonium-209 were determined.

Actinium-227 Separation Actinium-227 tracer was used in testing the ion exchange separation of that isotope from its daughter products. All of the daughter products were eluted by 1.75 M nitric acid. Actinium was eluted with 6 M nitric acid, and thorium-227 was eluted with ammonium acetate.

Half-Life of Plutonium-238 The half-life of plutonium-238 was determined by measuring the decay rate of two samples with Calorimeters 39 and 90. Each power measurement was corrected for other isotopes of plutonium, based upon the weight of the samples and analyses by mass spectrometry. After 590 days the grand mean of three half-life determinations was 87.48 years with an internal probable error of 0.04 year and an external probable error of 0.06 year; Birge's method, which indicates consistency of the mean, was used. Before correcting each power measurement, the apparent half-life of the samples was 88.6 years; therefore, the other isotopes, primarily plutonium-241, increased the half-life of the samples by 1.1 year. The corrections are probably accurate to 5%, which is equivalent to 0.06 year in the half-life. By propagation of errors, using the external probable error because it is larger, the half-life and probable error of plutonium-238 from this work is 97.48 ± 0.08 years.

ISOTOPE SEPARATION

Helium-3

Helium-3 Thermometry The thermomolecular pressure corrections to be used in helium-3 vapor pressure thermometry are being determined. Due to a system leak only a single datum point was obtained in a recent experiment. The datum point placed the thermomolecular pressure correction between 1/4 inch and 1/32 inch tubes at 0.180 torr. This value is higher than the 0.160 torr calculated from the Weber-Schmidt equation.

Superfluid Experiment A successful superleak and heat flush device was built and operated. Superfluid helium-4 was separated from its normal component and from helium-3 by filtering through a capillary packed with jeweler's rouge. Controlled heat aided the separation. A second experiment demonstrated that the phenomenon was reproducible and controllable.

Thermal Pump A thermal pump consisting of four alternately heated cylinders is being tested for filling cylinders with helium-3 gas purified by thermal diffusion. With feed pressures of 30 and 40 psig, final pressures of 115 and 140 psig, respectively, were obtained. Next, the pumping limit of the system will be determined by increasing the length of heating on each cylinder.

Carbon Isotope Separation Experiments are being performed to enrich carbon isotopes by converting methane to elemental carbon. Natural abundance methane was passed over heated platinum coil (1100-1200°C). The carbon recovery was 70-75% of the theoretical yield.

The extension of carbon-14 dating techniques by precise enrichment of this isotope in a Trennschaukel is being studied. At least five liters of enriched methane would be required for counting purposes to extend the dating technique to ten carbon-14 half-lives (ca. 58,000 years).

Neon Isotope Separation Fifty-five days were required to deplete 88% of the 55 liters of neon-20 in the neon-21 system. The columns are being equilibrated to allow the remaining neon-20 to be transported to the upper column where it can be isolated from the rest of the system.

Argon Separation A pump was added to the recirculating hot calcium purification system for argon-36 to increase the flow of gas through the trap. The impurity concentration at the top of the last stage has dropped from 90% to 2%.

Krypton Isotope Separation Krypton-78 and -80 have been enriched to 10% in the product. A krypton-85 product to feed ratio was found by internal gas phase proportional counting to be 0.46 ± 0.008 ; this value is equivalent to a krypton-85 depletion factor of 2.17.

Xenon Isotope Separation and Purification The eight-column, four-stage cascade thermal diffusion system product reached near equilibrium composition, and 470 ml of product was withdrawn. Then the system was revised to a five-stage (3-2-1-1-1) system.

An improved cleanup of xenon was obtained when nitrogen replaced helium as the carrier gas in the experimental chromatograph. An in-line solid state beta detector is being investigated for determining concentrations as low as 10^{-10} atom % krypton-85 in xenon.

Thermal Diffusion Research

Wire Heating by Alternating Current The neon isotope separation results using a 24-foot thermal diffusion column with a spring tension device and AC power for heating the center wire were compared with the separation with a similar column and AC power. The separation factors were similar.

Trennschaukel The Trennschaukel device for measuring the coefficient of thermal diffusion in gases has been accepted as satisfactory after having been repaired by the manufacturer. The flow rates were acceptable.

Thermal Diffusion Theory Preliminary results from calculations of the integrals for K_c and K_d were compared with McInteer's values in the literature. Since the 0.3% maximum deviation from the literature values was greater than expected, the program is being modified to include McInteer's interpolation technique.

ADHESIVES RESEARCH

Conductive Adhesives A polyurethane base conductive adhesive was formulated which is stable electrically at 160°F. Previously developed polyurethane base adhesives did not have this stability. Immediately after cure (16 hours at 110°F) the electrical resistivity of the formulation was 0.5 ohm-centimeter. After heating for two weeks at 160°F, the resistivity was 0.13 ohm-centimeter.

ANALYTICAL

Beryllium by Gamma Activation Analysis The geometry of the chamber used for irradiating beryllium samples and the guide tube were modified to prevent rotation of the irradiation chamber about its own axis. The neutron counting tubes were also lowered further into the paraffin thereby placing the center of their active area exactly in line with the beryllium during irradiation. These modifications have increased the count rate per gram of beryllium by a factor of two and eliminated the slight variation in count rate due to radial geometry.

Tritium Counting Analysis Investigations have been made on the feasibility of analyzing gas samples by scintillation counting. An anthracene solid scintillator was able to detect 1×10^{-3} mole % tritium in helium-3. With xenon gas as a scintillator to lower the detectable limit of tritium, samples of 1×10^{-4} to 5×10^{-5} mole % tritium in helium-3 have been successfully counted.

Coating Resistance to Thorium Residue A two-component epoxy coating which is being tested for use in storing thorium residues showed no deleterious effects after two months' exposure to alpha radiation.

RADIOELEMENTS RESEARCH

In support of other programs at Mound Laboratory basic and applied research on a number of radioelements is being conducted to determine physical properties, develop analytical techniques, and study the basic radiochemistry involved. Of particular interest are alpha emitters, their decay chains, their isotopes, and their chemical homologs.

URANIUM-234 SEPARATION AND PURIFICATION

Mound Laboratory is separating and purifying uranium-234 from aged plutonium-238 solutions by a combination of anion exchange and solvent extraction techniques. To date two aged plutonium samples have been processed and 84 mg uranium-234 recovered. A third sample containing 2 g uranium-234 is being processed through the anion exchange step. Cold work on the behavior of uranium on an anion exchange column and in a solvent extraction system was continued.

The remaining analyses on solutions from Run III were completed, and the data for the entire run are given in Table 1. The plutonium behavior was consistent with previous experience. The first two raffinates collected before the breakthrough were reasonably low in plutonium. After the breakthrough, washing with 7.2 *N* nitric acid decreased the plutonium levels until excessive gas on the column made backwashing necessary. The disruption of the resin bed caused a high plutonium level in raffinate 3R7, but the level went down in subsequent washings.

The uranium went through a maximum roughly corresponding to the plutonium breakthrough, then decreased as the washing progressed. Interestingly, the uranium also showed an increase in the backwashing step. Although the mass balance of the plutonium indicated less than 0.5% loss, this value will have to be confirmed by further experiments. The uranium mass balance showed a gain of 51 mg, or about 7%, which was within the estimated accuracy of the analysis.

Raffinates 3R2 through 3R6 were combined and evaporated to less than a liter. This solution will be held for further processing. Raffinates 3R1, 3R7, and 3R8 were combined with the first elutriate, 3E1, and will be recycled in a future ion exchange run. Therefore, the uranium fraction from Run III contained 7.2% of the total plutonium and 87.4% of the total uranium, while the plutonium fraction contained 82.0% of the plutonium and 3.2% of the uranium.

A solution assayed to contain 36.16 g plutonium and 548 mg of uranium was used as a feed solution in ion exchange Run IV. About five liters of wash solution was used to remove the uranium; then the plutonium was eluted with about four liters of 0.35 *N* nitric acid. The analytical results are not yet complete.

Cold work on the purification of uranium by anion exchange from a high nitrate salt, low nitric acid medium was continued. Earlier analytical results showed that the uranium-234 product contained major amounts of iron, copper and aluminum. Standard solutions of ferric nitrate and cupric chloride were prepared, and 20-40 ml of each solution was added to a series of uranium solutions adjusted to 1.6 *M* in aluminum nitrate and 0.3 *N* in nitric acid. The solutions were passed slowly through a Dowex 1X4 column; the column was washed first with 1.6 *M* $\text{Al}(\text{NO}_3)_3/0.3 \text{ N HNO}_3$, then with 6 *N* HCl to remove the impurities. Finally, the uranium was eluted with 0.1 *N* hydrochloric acid. In eight runs, from 99.2% to 100% (average 99.7%) of the copper was removed. Iron decontamination ranged from 97.7% to 99.6% with an average of 98.6%. However, uranium recoveries were only 90%.

The method showed adequate decontamination of iron and copper in addition to the excellent decontamination of iron and copper in addition to the excellent decontamination of aluminum reported previously. The method is relatively rapid, and the equipment is simple. The biggest disadvantage is the low uranium recovery.

Table 1

Results of Ion Exchange Run III (Sample 3)^a

Solution	Vol. (ml)	Pu (g)	U (mg)	Comments
3A & B	1600	24.23	241	7.1 N Feed
Recycle	799	1.805	423	7.2 N Recycle Raff.
		26.03	664	
3R1	915	0.013	0	Resin 50% loaded
3R2	920	0.158	113	Resin 85% loaded
3R3	936	0.757	279	Resin 90% loaded, some breakthrough
3R4	940	0.458	150	7.2 N Wash
3R5	951	0.338	66	7.2 N Wash
3R6	488	0.161	17	7.2 N Wash
3R7	944	0.631	31	Column Backwashed
3R8	446	0.353	11	7.2 N Wash
3E1	450	1.80	25	Elutriate
3E2-5	3680 ^b	21.26	23	Elutriate
TOTAL		25.93	715	

^aPu determined by alpha counting; U determined by modified PAN method (MLM-1183).

^bSolutions evaporated to less than a liter before analysis.

Solvent extraction with tributyl phosphate (TBP) was investigated as a possible purification procedure for uranium. Known amounts of uranium were adjusted to 30 ml in a solution of 1 M aluminum nitrate and 1 N nitric acid. The solutions were contacted three times with equal volumes of 20% TBP in kerosene; the mixtures were shaken for 15 minutes each time. Then the organic phases were stripped three times each day by shaking for 15 minutes with equal volumes of a stripping agent. When 0.35 N nitric acid was used as a stripping agent less than 30% of the uranium was recovered. A solution of 16.7 M urea in 2 N nitric acid was more effective in stripping the uranium. In eight experiments with 8 to 170 mg uranium, recoveries ranged from 95 to 100%, with an average of 97.3%.

POLONIUM

Macrochemistry of Polonium The optical absorption spectra of several hexahalopolonate(IV) complexes have been obtained using the $\text{Po}^{208}/\text{Po}^{209}$ recently purified at Mound Laboratory. The optical densities of solutions of polonium in approximately 1.5 M hydrohalic acids were measured in a Beckman DU spectrophotometer using the same acid concentrations as reference solutions. The hexachloro-, hexabromo-, and hexaiodopolonate(IV) complexes were prepared by dissolving polonium hydroxide in hydrochloric, hydrobromic, and hydriodic acids, respectively. The complexes were distinctively colored: PoCl_6^- was yellow-green, PoBr_6^- was orange-red, and PoI_6^- was blue-green. The color of the hexaiodopolonate(IV) anion was maintained even at room temperature, although Bagnall¹ gave the color as red-brown at 20°C. The red-brown

¹K. W. Bagnall, *The Chemistry of the Rare Radioelements*, New York, Academic Press, Inc., 1957, p. 72.

color may have been due to elemental iodine released by alpha-radiolysis of the solution, which contained the shorter half-life isotope polonium-210. This conclusion is supported by the gradual change in color of the hexaiodopolonate(IV) complex from green to red-brown over a period of several days.

The observed absorption spectra are shown in Figure 1, where the absorbance is plotted as a function of frequency. The absorption bands responsible for the observed colors of the complexes are plainly visible. The spectra were obtained using solution approximately $3 \times 10^{-5} M$ in polonium. An accurate determination of the polonium concentration is not possible because of the uncertainty in the half-life of polonium-209.

In any case, the molar extinction coefficients of the strong absorption bands in each of the three polonium complexes are of the order of 10^4 . The magnitude of the extinction coefficients indicates that they are charge-transfer bands, in which electrons in metal orbitals are excited to orbitals localized mainly on the ligands. Further work is in progress to determine the effect of iodide ion concentration on the relative absorption of the two absorption peaks observed in the PoI_6^{4-} .

Decay Scheme Studies The results of several alpha pulse-height analysis experiments have been combined with the results of recent alpha-gamma coincidence experiments to calculate the alpha particle energies of the several alpha groups in polonium-208 and polonium-209. The alpha groups and their energies are:

$$\text{Po}^{208} \alpha_0 = 5.110 \pm 0.005 \text{ Mev}$$

$$\alpha_1 = 4.198 \pm 0.015 \text{ Mev}$$

$$\text{Po}^{209} \alpha_0 = 4.861 \pm 0.005 \text{ Mev}$$

$$\alpha_1 = 4.602 \pm 0.015 \text{ Mev}$$

$$\alpha_2 = 4.308 \pm 0.015 \text{ Mev}$$

Figure 1. The Optical Absorption Spectra of Hexahalopolonate(IV) Complex Anions.

The results of the alpha-gamma coincidence experiments have completed the qualitative aspects of the decay schemes of both polonium-208 and polonium-209. Further work will now be directed towards determination of branching ratios and internal conversion coefficients. The tentative decay schemes for polonium-208 and polonium-209 are given in Figure 2. The discovery of the third alpha group of polonium-209 has clarified several problems which arose in the gamma-ray and conversion-electron spectra of the mixed isotopes. The three conversion-electron peaks observed at 530, 570 and 600 kev, and the broad gamma-ray peak at about 570 kev are assigned as shown in Figure 2. The observed spectra are attributed to the doublet at 530 and 600 kev in bismuth-208 and the gamma ray accompanying the third alpha group of polonium-209.

ACTINIUM-227 SEPARATION

Actinium-227 tracer was used in testing the technique of separating the isotope from its daughter products.² The actinium tracer was obtained from an aged sample in equilibrium with its daughter products. As shown in Figure 3 actinium-227 was completely separated from the radium group, which was eluted with 1.75 M nitric acid. Thorium eluted sharply in the ammonium acetate solution, although it may have started to elute in the 6 M nitric acid. Because counts were only made on drops of the eluate, the graph is meant only to indicate a trend in the elution, and not the precise elution curve.

HALF-LIFE OF PLUTONIUM-238

The half-life of plutonium-238 was determined to a greater degree of accuracy than the current values in the literature. The value used at present is 86.41 ± 0.3 years obtained by Hoffman, Ford, and Lawrence³ by the growth of plutonium-238 from its curium-242 parent. A value of 86.40 years was obtained at Mound Laboratory⁴ from specific activity measurements by counting and calorimetry. Other values in the literature are 89.59 ± 0.37 years by direct alpha decay measurements by Jaffey and-Lerner⁵ and 92 ± 2 years by plutonium-238 growth from curium-242 by Seaborg, James and Ghiorso.⁶

Because of the high degree of precision ($\pm 0.002\%$) obtainable on optimum samples with our present calorimeters, a half-life determined by direct decay over a period of a year or more would be resolved to a greater extent than any of the above values.

The plutonium was received at Mound Laboratory as plutonium nitrate solution on August 8, 1961. The mass analysis supplied with the shipment is given in the second column of Table 2. Since the neptunium was determined and reported separately, the percentages have been normalized to include the neptunium by dividing by the factor, 0.00735. The normalized values are listed in the last column of Table 2.

About May 1, 1962, the plutonium, without further purification, was precipitated from nitric acid with oxalic acid. The oxalate precipitate was dried and then calcined at 1500°C for 30 minutes in a RF furnace. It was assumed that any decay products which had grown into the plutonium were carried into the oxide and that the product was stoichiometric PuO_2 . Weighed quantities of the calcined oxide were doubly encapsulated in welded stainless steel containers.

²MLM-CF-63-11-221, pp. 34-35; MLM-CF-63-8-201, pp. 15-17.

³D. C. Hoffman, G. P. Ford, and F. O. Lawrence, *J. Inorg. Nucl. Chem.*, **5**, 6-11 (1957).

⁴MLM-1152, p. 20.

⁵A. H. Jaffey and J. Lerner, Reported in Argonne National Laboratory Report, ANL-4411 (1950).

⁶G. T. Seaborg, R. A. James, and A. Ghiorso, "The Transuranium Elements", *National Nuclear Energy Series*, Vol. 14-B New York, McGraw-Hill Book Co., Inc., 1949.

Figure 2. Tentative Decay Schemes of Polonium-208 and Polonium-209.

Figure 3. Separation of Actinium-227 on Dowex AG50W-X8 Resin (60°C).

Table 2

Mass Spectroscopic Analyses August 4, 1961,
of Plutonium-238 Half-life Samples

Isotope	Mass Analysis (wt %)	Normalized Values (wt %)
Pu ²³⁸	78.58	78.007
Pu ²³⁹	16.93	16.806
Pu ²⁴⁰	3.52	3.494
Pu ²⁴¹	0.82	0.814
Pu ²⁴²	0.145	0.144
Np ²³⁷	0.74	0.735
	100.735	100.000

A period of nine months had elapsed between the mass spectrograph analysis and the precipitation and weighing of the oxide samples. Therefore, the normalized percentages of Table 2 had to be corrected for the growth of daughter isotopes. The calculations are shown in Table 3. For a first approximation, the plutonium-238 half-life was taken to be 86.4 years. The last column of Table 3 lists the calculated percentages of each isotope at the time the two oxide samples were weighed. From the weight percentages of Table 3, an average molecular weight of 238.367 was calculated. If the oxide is MO₂, then the gravimetric

factor for the weight of metal is 0.881642. The total weights and calculated weights of each isotope are listed in Table 4.

It was desirable to calculate the power equation of the isotopes at the start of the growth of americium-241 from plutonium-241 which was assumed to be the time of chemical purification and mass analyses (August 4, 1961). Table 5 gives the extrapolated weight of each isotope at the time and was calculated by back-decaying the weights in Table 4.

The calculated power of each isotope at $t = 0$ is given in Table 6. Plutonium-241 is the only isotope having a daughter which affects the half-life results significantly. The half-lives of the other isotopes are so long

Table 3

Composition of Plutonium-238 Half-life Samples

Isotope	Half-life (mos.)	Wt % at $t = 0$	Wt % at $t = 9$ mo.
Pu^{238}	1.0369×10^3	78.007	77.539
U^{234}	2.976×10^6	0	0.460
Pu^{239}	2.69×10^5	16.806	16.806
Pu^{240}	7.896×10^4	3.494	3.494
Pu^{241}	1.56×10^2	0.814	0.782
Am^{241}	5.49×10^3	0	0.032
Np^{237}	2.64×10^7	0	nil
Pu^{242}	4.548×10^6	0.144	0.144
Np^{237}	2.64×10^7	0.735	<u>0.735</u>
			99.992

Table 4

Composition of the Plutonium-238 Samples by Weight
at Time of Weighing (May 1, 1962)

	Sample 1 (g)	Sample 2 (g)
Total weight oxide	1.6084	2.8058
Total weight of metal	1.4180	2.4737
Pu^{238}	1.0996	1.9182
U^{234}	0.0065	0.01138
Pu^{239}	0.2383	0.4158
Pu^{240}	0.0495	0.0864
Pu^{241}	0.0111	0.0193
Am^{241}	0.00045	0.00079
Pu^{242}	0.00204	0.00356
Np^{237}	0.01042	0.01818

that the power contribution is assumed to be constant. Equation 1 represents the decay scheme of plutonium-241 as used in the corrections.⁷

The average energy of the plutonium-241 beta in Equation 1 was determined by Shliagin.⁸

Table 5

Extrapolated Composition of the Plutonium-238 Half-life
Samples by Weight as of t = 0 (August 4, 1961)

	Sample 1 (g)	Sample 2 (g)
Pu ²³⁸	1.10604	1.92945
Pu ²³⁹	0.23829	0.41569
Pu ²⁴⁰	0.04954	0.08642
Pu ²⁴¹	0.01154	0.02013
Pu ²⁴²	0.00204	0.00356
Np ²³⁷	0.01042	0.01818

Using the weights and power of plutonium-241 in Tables 5 and 6 which correspond to t = 0 of August 4, 1961, the power curve in microwatts as a function of time in days has been calculated and is given by Equations (2) and (3).

$$W_1(\text{Pu}^{241}) = 1283.8 [\exp(-4.144 \times 10^{-6}t)] - 1229.0 [\exp(-1.453 \times 10^{-4})] \text{ microwatts} \quad (2)$$

$$W_2(\text{Pu}^{241}) = 1.7445 (W_1) \text{ microwatts} \quad (3)$$

⁷Half-lives in Eq. (1) are weighted mean values of the following:

Pu ²⁴¹ : 13.3 ± 0.3 yrs.	H. L. Smith, <i>J. Inorg. and Nuclear Chem.</i> , 17 , 178 (1961).
13.24 ± 0.24	G. G. George and D. E. Green, <i>J. Inorg. and Nuclear Chem.</i> , 13 , 192 (1960).
12.95 ± 0.28	B. Rose and J. Milsted, <i>J. Nuclear Energy</i> , 2 , 264 (1956).
13.0 ± 0.2	D. R. Mackenzie et al., <i>Phys. Rev.</i> , 90 , 328 (1953).
12.8 ± 0.3	J. Mech and G. Pyle, ANL-4296, Dec. 1953.
13.06 ± 0.11 yrs.	(Weighted Average)
Am ²⁴¹ : 498 ± 25 yrs.	B. B. Cunningham, <i>National Nuclear Energy Series</i> , Vol. 14-B, 1949.
470 ± 8	B. G. Harvey, <i>Phys. Rev.</i> , 85 , 482 (1952).
457.7 ± 1.8	P. Graf and L. Goda, <i>J. Inorg. and Nuclear Chem.</i> , 7 , 199 (1958).
458.8 ± 0.5	Hall and Markin, <i>J. Inorg. and Nuclear Chem.</i> , 4 , 137, (1957).
458.11 ± 0.48	(Weighted Average)

⁸K. N. Shliagin, *Sov. Phys. JETP*, **3**, 663 (1956).

Table 6

**Calculated Power of Each Isotope in the Plutonium-238
Half-life Samples as of August 4, 1961**

	Sample 1 (microwatts)	Sample 2 (microwatts)
Pu ²³⁸	628,275	1,096,005
Pu ²³⁹	455.0	793.7
Pu ²⁴⁰	347.5	606.2
Pu ²⁴¹	54.8	95.5
Pu ²⁴²	0.23	0.41
Np ²³⁷	0.21	0.37

The power contributions from the long-lived isotopes, plutonium-239, plutonium-240, plutonium-242, and neptunium-237 are essentially constant. From Table 6, the total is 802.9 microwatts for Sample 1, and it is 1400.7 microwatts for Sample 2.

The complete half-life results are shown in Table 7. The results with calorimeter 90 are much better than with Calorimeter 39. The reason is almost entirely due to the improved methods of operation used with Calorimeter 90; *i.e.*, use of a constant current controller, shunting one arm of the bridge in order to record the bridge potentials, and automatic loading in a hermetically sealed system. The reason for the poorer results of Sample 2 as compared to Sample 1 is not yet known; both samples were run in Calorimeter 90. Except for the calorimeter, the probable error per observation for Sample 2 should have been 1.745 times greater than for Sample 1, or 13 microwatts. Instead, the probable error was 17 microwatts. When the two samples were measured simultaneously, the increase in percentage error was even greater. Convection effects in the air gap of the calorimeter may be the cause, since convection tends to increase to the 1.5th power of the temperature difference.

Table 7

**Half-life Results of Plutonium-238 After Subtracting
Power Contribution from Other Isotopes**

Sample	Calorimeter	Number of Observations	Time Span (days)	Power of Pu ²³⁸ as of Dec. 12, 1962 (microwatts)	Probable Error Per Single Observation (microwatts)	Half-life of Pu ²³⁸ (yrs.)	Probable Error in Half-life (yrs.)
2	39	19	591	1,134,595	67	86.70	0.29
2	90	40	407	1,134,559	17	87.42	0.07
1	90	47	479	650,326	7.4	87.54	0.05

NOTE: Weighted Grand Mean Half-life = 87.48 yrs.

Internal Probable Error = 0.04 yr.

External Probable Error = 0.06 yr.

The power ratio of the two samples by Calorimeter 90 in Table 7 is 1.7446, which can be compared to the weight ratio in Table 4 of 1.7445. Hence, one can assume that the two samples have the same composition. The weighted grand mean half-life of 87.48 years with internal and external consistencies of 0.04 and 0.06

year indicates that the means are consistent. Of course, the probable errors do not reflect to any extent a possible error in the isotope corrections. This fact can be shown by solving for the apparent half-life of the sample without corrections. With 41 data points, half-life results were calculated for Sample 1, Calorimeter 90, with and without the corrections (Table 8). The isotope corrections change the half-life from 88.556 to 87.453 years, or 1.103 years. If the corrections are in error by 5%, the half-life will be in error in the corrections; therefore, by propagation of errors, the probable error in the present half-life of 87.48 years is:

$$P.E. = \sqrt{(0.060)^2 + (0.055)^2} = 0.081 \text{ year}$$

The half-life measurements will be continued and, in time, the data will be solved for one or more constants in the equation of the isotope correction. Thus, less dependence will be placed upon the mass spectrometer analyses.

Table 8

**Plutonium-238 Half-life Results, Sample 1, Calorimeter 90,
41 Data Points, Before and After Applying Isotope Corrections**

	Initial Power Feb. 15, 1963 (microwatts)	Half-life (yrs.)	Probable Error (yrs.)
With correction	650,328.5	87.453	0.081
Without correction	651,253.5	88.556	0.079

ISOTOPE SEPARATION

Processes are being developed for separating and purifying the isotopes of a number of elements including the noble gases and carbon. Potential sources of supply of these materials are being evaluated.

HELIUM-3

Helium-3 Thermometry Mound Laboratory is cooperating in an international effort to establish a helium-3 temperature scale in the range of 0.3° to 3.2° K. The thermomolecular pressure drop set up in a tube possessing a temperature gradient is being determined at Mound Laboratory.

An experiment was made with helium-3 in both the vapor pressure bulb and the inner cooling bath of the triple dewar thermometer system. Because of a leak between the outer helium-4 bath and the inner vacuum jacket only a single datum point was obtained. The datum was obtained with helium-3 vapor not in equilibrium with its liquid phase; there was an observed thermomolecular pressure difference of 0.180 torr between the 1/4-inch and 1/32-inch vapor pressure tubes at the warm end; a total pressure of 1.73 torr was measured through the 1/4-inch tube. This value agrees with similar measurements made previously at Mound Laboratory, but it is greater than the 0.160 torr predicted by calculations with the Weber-Schmidt equation.

Superfluid Experiment The superfluid properties of liquid helium-4 below 2.2° K may be used to achieve a partial separation of helium-3 from helium-4. Since the light isotope does not exhibit superfluidity, it is possible to devise a "superleak" which will pass the fraction of helium-4 atoms which are in the lowest quantum mechanical energy level, or ground state. The separation is enhanced by applying heat to the downstream side of the superleak to excite the helium-4 atoms to a normal energy level, thus preventing backstreaming through the leak. The process is particularly suited to enriching mixtures containing a low concentration of helium-3, such as the raffinate gas from thermal diffusion columns.

A simple device (Figure 4) was fabricated to qualitatively test the superleak and heat flush concepts. The superleak consists of a capillary packed with jeweler's rouge. The entire assembly shown in Figure 4 was immersed in a liquid helium-4 bath. Two successful tests were made with the apparatus.

Test 1 Both sides of the superleak were evacuated, and the jeweler's rouge was allowed to outgas for several days. Helium-4 at approximately 300 torr was admitted into the copper cold finger while a vacuum was maintained on the heater side. There was little leakage of gas through the rouge. The cryostat was loaded with liquid helium-4, and the temperature was reduced to about 2.8° K by pumping on the bath. The helium sample then condensed in the cold finger. The condensation was observed indirectly as the pressure in the cold finger equilibrated with the bath pressure. There was no flow through the superleak.

The bath pressure was reduced so that the temperature dropped to about 1.4° K, well below the lambda point (2.19° K). No immediate flow was observed. However, after three to four minutes, a liquid appeared on the heater side of the leak, and the liquid level rapidly rose to a point slightly below the heater, then stopped. Power was then applied to the heater in steps of five milliwatts. At approximately 15 milliwatts the liquid helium level started to rise again, and it peaked at 25 milliwatts. A greater heat input caused boil-off and a drop in the level.

With the heater on, the bath temperature was raised above the lambda point. The liquid level was not under observation at this point. After the cryostat reached room temperature, a pressure of approximately 200 torr remained on the cold finger side, indicating that one-third of the helium had been driven through the leak.

Test 2 The same procedures were followed as in Test 1 except that the feed gas contained approximately 0.1% helium-3 (mass spectrometer results of the test will be reported later) at 380 torr. The experi-

Figure 4. Superleak Assembly (The entire assembly is immersed in a liquid helium-4 bath during the experiments).

ment was performed as in Test 1 although higher heat inputs were required to move the liquid through the superleak. A second heater was installed slightly above the first (as shown in Figure 4) to raise the liquid level on the heater side. It was possible in this test to drive the level above the second heater.

At this point, the bath temperature was raised from 1.4°K to 4.2°K while the liquid level in the heater chamber was being observed. The flow began again but in the opposite direction, and the major part of the separated liquid was lost. During the short time required to raise the bath temperature above the lambda point, the temperatures were reversed on either side of the leak. That is, the temperature of the cold finger rose rapidly with the bath due to the good thermal conductivity of the copper, while the fluid in the thick-walled glass tube remained below the lambda point. At room temperature 322 torr of helium remained on the cold finger side although obviously more helium-4 had been transported through the leak before the reverse flow began.

Helium-3 Thermal Pump A thermal loading pump is being tested for filling cylinders with helium-3 purified by thermal diffusion.⁹ The system consists of four cylinders which are alternately heated to increase the gas pressure. This type of pump would be superior to the present mechanical compressors because there would be no problems of contamination from the pump itself. Table 9 shows the data on runs at higher feed pressures. These pressures were used to simulate the effect of another heating vessel immediately downstream of the feed cylinder. The load pressure was still increasing by 1-2 psig per minute at the end of the cycles listed. The maximum pressure attainable in the above cases would be about 20-30 psig higher. Safety controls are being installed to allow longer runs.

In the case of the 40 psig feed, the load pressure at the end of the 28th cycle was 149 psig instead of 160 psig because of several power interruptions during electrical current measurements.

Table 9

Thermal Pump Data

Feed Pressure (psig)	Application of Current to Each Heater (min)		Approximate Heater Temperature (°C)		Load Pressure (psig)
	Nos. 1, 2, and 3	No. 4	Nos. 1, 2, and 3	No. 4	
30 ^a	1.5	1.8	370	420	115
40 ^b	1.5	1.8	370	420	149

^a24 cycles of 12 min. each.

^b28 cycles of 12 min. each.

Current was applied to the No. 4 heater for 1 minute and 50 seconds, after which time the sheath had reached about 400°C. This longer time of applied current was used only on one heater to determine if the heater could be operated this long without any adverse effects. The element has operated for 54 cycles without any noticeable loss of efficiency.

CARBON ISOTOPE SEPARATION

The objectives of the carbon-13 program are the preparation of gram quantities of 90% pure carbon-13, the evaluation of carbon monoxide and methane as feed materials for the thermal diffusion separation systems, and the evaluation of various other separation methods, such as chemical exchange and distillation.

⁹MLM-1183, p. 8.

Conversion of Methane to Carbon Experiments are being performed on converting methane to elemental carbon. Natural abundance methane was passed over a platinum coil heated to 1100° to 1200°C. Unreacted methane was in the range of 70 to 75% of the theoretical yield. Loss of carbon resulted from (1) mechanical loss and (2) formation of ethylene, ethane and higher hydrocarbons.

Carbon-14 The feasibility of extending carbon-14 dating techniques by a quantitative enrichment of the isotope in a Trennschaukel was studied. At least five liters of enriched methane would be required to extend the carbon-14 dating to ten half-lives (ca. 58,000 years).

NEON ISOTOPE SEPARATION

The one-one overlap system enriched neon-20 to about 99.7% at a rate of 80 ml per hour, and neon-22 to about 99.8% at 5 ml per hour; it also separated in intermediate stream of about 46% neon-20, 3% neon-31 and 51% neon-22 at a rate of 5 ml per hour.

Fifty-five days were required to deplete 88% of the 55 liters of neon-20 in the neon-21 system. Approximately 2.2% neon-20 is left in the reservoir and 9.8% in the two columns, which are, respectively, 0.61 liter and 5.9 liters. The reservoir concentrations are 2.1% neon-20, 5.9% neon-21, and 82% neon-22 in the 27.6 liters left in the reservoir. Mass spectrometer results show that the neon-21 peaks in the middle of the cascade and is enriched there to about 20%.

The columns are being equilibrated to allow the remaining neon-20 to be transported to the upper column where it can be isolated from the rest of the system. The gas in the reservoir and the lower column will then be recovered and used as feed in the second step of the experiment.

ARGON SEPARATION

A stainless steel trap was placed in operation with a flow meter in the trap circulating line to monitor convective flow at the top of the last stage in the argon system.¹⁰ This flow was inadequate for proper circulation of the gas through the calcium. Therefore, a single-end magnetic pump was inserted in the trap line. It maintained a flow of about 75 ml per minute through the trap and across the top of the last column stage.

The impurity concentration at the top of the last stage has dropped from 90% to about 2% with the argon-20 at 0.02%. This concentration indicated efficient cleanup and elimination of the argon-40 from the trap by forced circulation through the last stage top.

KRYPTON ISOTOPE SEPARATION

The two-column, hot-wire thermal diffusion cascade system with a reservoir at the bottom is processing the twenty-second batch of krypton to enrich the product to a krypton-78 and -80 concentration of about 10%. At the end of this run, about 45 liters of product will have been accumulated.

The product gas from Run 22 will be used for experimental runs for stage 2 to separate 30% krypton-78 and -80 product and then for stage 3 to separate 56% krypton-78 and -80 product. These experimental runs will furnish data for the correlation between theoretical and actual performance.

The krypton-85 content of the product gas was compared to that of natural krypton gas (which was used as the feed). The product to feed ratio was found by internal gas phase proportional counting to be 0.46 ± 0.008 ; this value is equivalent to a krypton-85 depletion factor of 2.17.

¹⁰See illustration in MLM-1192.

XENON ISOTOPE SEPARATION AND PURIFICATION

Thermal Diffusion The eight-column, four-stage cascade thermal diffusion system product reached near equilibrium composition at the following isotopic concentrations:

Total Xe	99.91%
Xenon-131	0.65%
Xenon-132	2.09%
Xenon-134	14.54%
Xenon-136	82.72%

About 470 ml of this gas was removed from the swing reservoir at the product end of the system.

The four-stage system was then revised to a five-stage system with a 3-2-1-1-1 arrangement as shown in Figure 5. The system has been started with new feed. The present swing cycle shows adequate net transport between stages on a pressure basis. Analytical data are being obtained.

Figure 5. Xenon Five-stage Swing Cascade System [Sample Ports are Located at the Top and Bottom of Each Column].

Experimental Chromatograph A series of runs were performed in the experimental separation of krypton from xenon (Table 10). A marked increase in cleanup occurred when nitrogen was used as the carrier gas. A heavier molecular weight carrier gas allows less diffusion of sample components. Nitrogen was selected as a carrier gas because it is heavier than helium and would not be frozen in the cold traps. Nitrogen could not be used in an analytical column, however, because of the difficulty of distinguishing xenon from nitrogen with a thermal conductivity detector. Therefore, to determine when to change traps, the elution of krypton-85

was monitored (see below). This preliminary work indicated that nitrogen shows the most promise for a highly efficient carrier gas in purifying xenon. Nitrogen is less expensive and more readily available than helium and requires less time to make a run.

Krypton-85 Monitor The feasibility of an in-line solid-state beta detector is being examined. Potential uses for such a detector include the measurement of krypton-85 in krypton and krypton-85 in xenon. It is not expected that this detector would have the sensitivity and precision of internal gas phase proportional counting, but such an arrangement would allow concentration measurements down to a level of approximately 10^{-10} atom % krypton-85 without collecting and removing samples for analysis.

Table 10
Comparison of Helium and Nitrogen as Carrier Gases in the
Chromatographic Separation of Krypton-85 from Xenon

Experiment Number	Carrier Gas	Cleanup (Xe in Feed/ Xe in Trap)	Kr Retention Time (min.)	Time till Xe Peak (min.)	Time Traps switched ^a (min.)	Recovery in Xenon Trap (%)
1	He	1120	33.5	41	—	70 ^b
2	He	1202	36	43	—	74
3	N ₂	2625	3	a	22	28 ^b
4	N ₂	3430	3	a	11	79
5	N ₂	5560	3	a	13	71

^aThe thermal conductivity detector was not able to detect xenon at the experimental conditions maintained. These conditions were set to make these runs comparable to those using helium as the carrier gas. Since the xenon peak was not observable, the xenon trap was placed in the line when the krypton peak approached the normal base line. The time until this change was made is shown.

^bBecause of a loss of gas in the krypton trap, the total recovery could not be calculated. These figures are, therefore, estimated xenon recoveries.

THERMAL DIFFUSION RESEARCH

Wire Heating by Alternating Current The neon isotope separation results using a 24-foot thermal diffusion column with a spring tension device and alternating current for heating the center wire are shown in Table 11. A comparison of these results with those from an experiment under the same conditions (except that direct current was used for heating the center wire) is shown in Table 12; the two methods were comparable.

To complete this set of experiments, an additional run using alternating current with a mercury well is planned.

Trennschaukel The Trennschaukel, or swing separator, will be used to measure the thermal diffusion coefficient of binary mixtures of gases in the temperature range from -40°C to 1000°C. This range will overlap the low region where some data have been obtained, and will extend measurements up to column hot-wire temperatures where measurements have not yet been made.

Following extensive repairs the Trennschaukel device was accepted from the manufacturer as satisfactory. The flow rates are now acceptable as shown in Figure 6.

Table 11

Comparison of Data for Neon Isotope Separation using
Spring Tension Device with AC and DC Power

Time (hrs.)	Separation Factor	
	Direct Current	Alternating Current
24	10,700	17,700
28	13,000	13,600
33	14,300	—
34	—	17,400
46	13,500	—
48.5	—	15,100

Figure 6. Trennschaukel Flow Rates.

Thermal Diffusion Theory A rigorous theory for the thermal diffusion column is being developed. One feature of this theory is that the dependence of the transport properties on the composition of the isotopic mixture is being taken into account. This composition dependence was not considered in the earlier theory of Jones and Furry. Another feature of the theory is that it allows for a variation in the wire temperature arising from the change in thermal conductivity of the gas.

Collision integrals for the Lennard-Jones potential were used in checking the computer program which calculates the integrals for the quantities K_c and K_d . McInteer¹¹ calculated the integrals for K_c and K_d for

¹¹B. B. McInteer, *J. Chem. Phys.*, **33**, 570 (1960).

this potential. The maximum deviation between results calculated in our program and those given by McInteer is less than 0.3% (in most cases, the deviation is much less than this). Since McInteer stated that his results were accurate to 0.01%, the 0.3% deviation is larger than would be expected. It is thought that the deviation arises because our program uses an interpolation technique different from that which McInteer used to obtain intermediate values of the collision integrals. The program is currently being modified to use the McInteer interpolation technique.

Table 12

**Neon Isotope Separation using Alternating Current in 24-Foot
Center Wire Thermal Diffusion Column with Spring Tension Device**

Sample	Concentration (mole%) of Sample taken at									
	0 hrs.		24 hrs.		28 hrs.		34 hrs.		48.5 hrs.	
	(Column 1)		(Column 2)		(Column 3)		(Column 4)		(Column 5)	
	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top
Total Ne	99.40	99.50	—	—	—	—	—	—	97.78	89.59
Ne ²⁰	51.96	52.42	4.47	99.85	4.39	99.82	4.23	99.85	4.22	99.85
Ne ²¹	0.19	0.16	0.16	0.03	0.17	0.02	0.13	0.02	0.12	0.00
Ne ²²	47.85	47.42	95.37	0.12	95.44	0.16	95.64	0.13	95.65	0.15
H ₂	0.24	0.17	—	—	—	—	—	—	0.00	10.38
He	0.00	0.00	—	—	—	—	—	—	0.00	0.00
H ₂ O	0.00	0.00	—	—	—	—	—	—	0.01	0.01
N ₂	0.36	0.32	—	—	—	—	—	—	2.17	0.01
O ₂	0.00	0.01	—	—	—	—	—	—	0.01	0.01
Ar	0.00	0.00	—	—	—	—	—	—	0.01	0.00
CO ₂	0.00	0.00	—	—	—	—	—	—	0.02	0.00
Separation Factor	—		17,700		13,600		17,400		15,100	

ADHESIVES RESEARCH

Adhesives are being developed for specialized applications. The adhesives must have satisfactory working and curing characteristics; they must retain flexibility at low temperatures and adequate tensile strength at elevated temperatures.

CONDUCTIVE ADHESIVES

A polyurethane base conductive adhesive was formulated which is stable electrically at 160°F. Previously developed polyurethane base adhesives did not have this stability. The formulation was as follows: Adiprene L-167, 15.2 parts (by weight); butyl glycidyl ether, 3.8 parts; methylene-bis-orthochloroaniline (MOCA), 2.2 parts, Continex CF carbon black, 7.0 parts; and J-2 silver powder, 71.8 parts. Immediately after cure (16 hours at 110°F) the electrical resistivity of the formulation was 0.5 ohm-centimeter. After heating for two weeks at 160°F, the resistivity was 0.13 ohm-centimeter. The plug tensile strength of the cured formulation was 600 psi, and its peel strength was 15 pounds per inch.

ANALYTICAL

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

BERYLLIUM BY GAMMA ACTIVATION ANALYSIS

The geometry of the antimony-124 irradiation chamber and guide tube in the gamma activation equipment was modified.¹² A slot was placed in the irradiation chamber along its vertical axis, and the quartz guide tube was replaced by a Lucite tube with a matching vertical flat. With this arrangement, rotation about the center axis of the irradiation chamber, which caused a slight variation in count rate, was eliminated.

The neutron detection tubes were also lowered further into the paraffin drum so that the center of their active areas is at the same level as the beryllium vial during irradiation. This modification increased the count rate per gram beryllium by a factor of two.

Two beryllium lots were analyzed by gamma activation. The results by gamma activation and wet chemical analysis are as follows:

Test	Beryllium By Gamma Activation (%)	Beryllium By Wet Chemical Analysis (%)
1	98.21	98.30 98.01
2	<u>98.27</u> 98.24	<u>98.37</u> 98.23
3	98.78	98.48 98.26
4	<u>98.72</u> 98.75	<u>98.58</u> 98.44

TRITIUM COUNTING ANALYSIS

Investigations have been made on the feasibility of analyzing radioactive gas samples by beta scintillation counting. An initial attempt was made using a solid, thallium-activated sodium iodide crystal (1/4 inch thick) sealed in a glass vacuum counting chamber which was coupled to a photomultiplier tube. Helium-3 gas samples ranging from 1×10^{-2} mole % tritium could be counted.

Because of its better response to beta radiation, an anthracene crystal was used to replace the thallium-activated sodium iodide crystal. With this arrangement, tritium in helium-3 was counted successfully to about 10^{-3} mole %. Krypton-85 in xenon was counted in concentrations as low as 5×10^{-10} mole %. This suggested that xenon, being a scintillator itself, was responsible for the good response in the krypton-85 counting.

Xenon gas, low in krypton-85 content, was obtained and used as a gaseous scintillator in helium-3 - tritium mixtures. With xenon as a scintillator samples of 1×10^{-4} to 5×10^{-5} mole % tritium in helium-3 have been successfully counted at a total pressure or 25 mm Hg.

¹² MLM-1179, pp. 37-39.

COATING RESISTANCE TO THORIUM RESIDUE

A material for coating concrete is being sought for use in storing thorium residues containing approximately 50% moisture.¹³ There was no apparent deleterious effect on a two-component epoxy coating after two months' exposure to polonium alpha radiation. The two component epoxy also showed no effect on being in distilled water or in a 50% thorium slurry.

¹³ MLM-1183, p. 21.