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SUMMARY

ALPHA AND NEUTRON SOURCES

Neutron Measurements

Gauss' Quadrature Formula To determine the total neutron emission rate of a source whose emission is not isotropic, it is necessary to integrate the neutron flux over 4π geometry. The accuracy of Gauss' quadrature formula for evaluating this integral was determined. The basic counting integral was evaluated in three different ways, one of which was a comparison to Simpson's Rule. Gauss' method was determined to be accurate and less time-consuming than Simpson's Rule.

Neutron Yields of PoBe Sources A comparison was made between the measured neutron yields of PoBe sources recently fabricated at Mound Laboratory and values previously reported in the literature. The best values were obtained from recently fabricated sources, which had a maximum yield of $(70 \pm 2) \times 10^{-6}$ neutrons per polonium alpha particle. Literature values ranged from 50×10^{-6} to $(80 \pm 16) \times 10^{-6}$ neutrons per polonium alpha particle.

ISOTOPE SEPARATION

Helium-3

Helium-3 Feed Gas Purification The length of the charcoal trap used to purify helium-3 feed gas prior to final enrichment by thermal diffusion was increased from 28 to 48 feet. This trap reduced the tritium content of the gas to 6.14×10^{-7} mole %.

Vapor Pressure Thermometry The Weber-Schmidt equation was investigated to determine the effect of the sensing tube radius on the thermomolecular pressure gradient in the helium vapor pressure thermometer. With a tube radius of approximately 0.025 cm, a change in radius of 0.01 cm can produce a maximum pressure deviation of approximately 80 microns of Hg. Since this deviation could represent as much as 50% of the total thermomolecular pressure gradient, it was necessary to accurately determine the radius of the 1/32-inch tube, thus eliminating a possible variable from the experimental work. The radius of the tube was 0.0249 ± 0.0006 cm. The ± 0.0006 -cm deviation can produce a maximum error of only about 2.5% in the data. Measurements of the difference in thermomolecular pressures in this 1/32-inch tube and a 1/4-inch tube were made using both equilibrium and nonequilibrium helium-4. The measurements agreed with earlier data obtained at Mound Laboratory; however, there is an unexplained discrepancy between these data and values determined by the Weber-Schmidt equation.

Superfluid Experiment Five experiments were performed in which helium-3 in dilute helium-3/helium-4 mixtures was enriched from 0.09% to 2.05% by filtering superfluid helium-4 through jeweler's rouge. A simple heat-flush technique was developed for preserving the separation at the end of the experiment.

Argon Isotope Separation Thirty-three days after the argon thermal diffusion system was started up with natural abundance feed gas the fourth stage top concentration was 99.55 mole % argon-35.

Xenon Isotope Separation and Purification

Thermal Diffusion The eight-column, five-stage, swing cascade thermal diffusion system was operated at 170 torr and at a wire temperature of 850°C to enrich xenon-136. At the bottom of the last stage the xenon-136 concentration was 81.71%. A light fraction from a previous xenon separation contained 2.66% krypton impurity. The krypton impurity in part of the xenon product was reduced to 0.30%, and the xenon concentration was increased to 20.88% in a two-column cascade thermal diffusion system.

Experimental Chromatograph The 2.66% krypton impurity in part of the xenon mentioned above was separated by gas chromatography. After this purification no krypton could be detected in the product by chromatography.

Xenon Tube Bundle A 24-column thermal diffusion system with an active length of 12 feet is being constructed. A prototype column was used for static separation of a mixture of argon isotopes at 2,500 and 3,500 torr. At the bottom of the system the argon-40 concentration was greater than 99%.

Thermal Diffusion Research

Center Wire Heating by Alternating Current Neon isotopes were experimentally separated by thermal diffusion using alternating current for heating the center wire; a mercury well was used at the bottom of the column. No wire vibration was visible at a wire temperature of 800°C.

Carbon Isotope Separation

Thermal Diffusion Enriched methane was used as feed for the 11-column, 9-stage thermal diffusion cascade. Approximately 18 g carbon-13 was accumulated in the form of methane. Isotopic purity of this product ranged from 90 to 94% carbon-13 in total carbon. The chemical purity of the product methane was 95 to 98% with nitrogen as the major impurity.

Conversion of Enriched Methane to Barium Carbonate In order to supply carbon-13 in the form of barium carbonate, a system has been built to make the conversion from methane. Enriched methane was burned in oxygen over a heated platinum filament. The resulting carbon dioxide was absorbed in a barium hydroxide solution, and barium carbonate was precipitated. Test runs with natural abundance methane showed complete recovery of the carbon as barium carbonate.

ADHESIVES RESEARCH

Conductive Adhesives Flexane-30, a two-part polyurethane potting material was evaluated as a matrix for conductive adhesives. Although the seven formulations prepared exhibited good low temperature flexibility and peel strength, tensile strength (110-200 psi) and electrical resistivity (>4 ohm-cm) were not satisfactory.

Three commercial silicone adhesives were filled with silver powder and evaluated as conductive adhesives. Peel strengths of all materials were poor. Attempts to increase the peel strength of LTV-602 adhesives by the addition of carbon black and three different tackifiers were unsuccessful.

ANALYTICAL

Low-level Krypton-85 Counting A study was made to determine whether krypton-in-xenon gas standards could be reused in calibrating proportional counting chambers. During the counting procedure the krypton-85 content of the gas was reduced from 2.4×10^{-10} atom % to 1.2×10^{-11} atom %. Thus, the gas standard cannot be reused. The gas is being analyzed to determine whether there was a change in isotopic ratio of the mixture.

RADIOELEMENTS RESEARCH

Actinium-227 Separation Actinium-227 on the tracer level was satisfactorily separated from its daughter products by ion exchange on Dowex AG50W-X8. The actinium was eluted in the 4 M HNO₃ fraction, as confirmed by alpha energy analysis.

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 has been processed through the anion exchange step resulting in a solution which contains 1.94 g uranium (87% recovery) and 1.20 g plutonium (1.1% of original). A final purification step was applied to the uranium product 5 HD. Solvent extraction techniques with tributyl phosphate are being developed. Sodium carbonate and hydroxylamine hydrochloride are being studied as stripping agents in "cold" work related to this separation.

ALPHA AND NEUTRON SOURCES

Mound Laboratory is responsible for producing alpha and neutron sources, manufactured from polonium-210 and plutonium-239, which cannot be produced by American industry at the present time. The techniques of fabricating these unusual sources are being developed and publicized.

NEUTRON MEASUREMENTS

Gauss' Quadrature Formula To determine the total neutron emission rate of a source whose emission is not isotropic, it is necessary to integrate the neutron flux over 4π geometry. In the case where a point detector is used to obtain counting data for a source whose emission is cylindrically symmetrical, it is sufficient to obtain data in one plane (containing the source axis of symmetry) as a function of the angle between the source axis of symmetry and the source-detector axis (θ). The problem then becomes one of selecting the values of θ for which counting data are to be obtained and evaluating the integral,

$$\int_0^\pi \dot{A}(\theta) \sin \theta d\theta,$$

where $\dot{A}(\theta)$ is the measured counting rate at angle θ . Gauss' quadrature formula has proven to be a satisfactory method of evaluating this integral. An earlier check on the accuracy of this method was made by using an expression of the type,

$$\dot{A}(\theta) = a + b \cos 2\theta,$$

to approximate the flux distribution about a source. This earlier check indicated that Gauss' formula gives good results. It was considered desirable to make a more detailed check by obtaining a more exact expression for $\dot{A}(\theta)$. A 24-point harmonic analysis was made of detailed counting data for source M590 to obtain the constants in the cosine series,

$$\dot{A}(\theta) = \sum_{n=1}^{n=12} a_n = b_n \cos n\theta.$$

The basic counting integral in the preceding paragraph was then evaluated in three ways:

1. By substituting the cosine series into the integral and integrating directly the product of the cosine series by $\sin \theta$; the determined value was 1509.4.
2. By first evaluating the cosine series at the angles required for Gauss' method, and then using Gauss' method to evaluate the integral; the determined value was 1509.7 (7 data points in a 180-degree interval).
3. By using Simpson's Rule and the raw counting data (36 data points in a 180-degree interval); the determined value was 1509.2.

The close agreement between 1 and 3 shows that the derived cosine series is a good approximation of the flux distribution function. The agreement between 2 and 1 shows that Gauss' method is accurate as well as considerably less time-consuming than Simpson's Rule.

Neutron Yields of PoBe Sources A comparison was made between the measured neutron yields of PoBe sources, a recently calculated value, and values previously reported in the literature. The maximum measured yield of sources recently fabricated at Mound Laboratory is $(70 \pm 2) \times 10^{-6}$ neutrons per polonium alpha particle. Using the reaction cross-section data of Gibbons and Macklin¹ and the stopping cross-section data of Bader et al.,² a yield of 64×10^{-6} neutrons per polonium alpha particle was calculated.

Runnalls and Boucher³ obtained an empirical formula for the yields of alpha-Be sources with thick targets, and from this formula calculated the maximum yield of a PoBe source as 67×10^{-6} neutrons per polonium alpha particle (with a possible error of about 6%). Earlier reported values are $(80 \pm 16) \times 10^{-6}$ by Roberts;⁴ $(73 \pm 22) \times 10^{-6}$ by Segre and Wiegand;⁵ and 50×10^{-6} by Anderson.⁶

It would appear that the best value to date for the thick target yield of a PoBe source of relatively small dimensions (0.5 inch diameter x 0.5 inch long) is that obtained from measurements made of actual sources fabricated here, $(70 \pm 2) \times 10^{-6}$ neutrons per polonium alpha particle.

¹J. H. Gibbon and R. L. Macklin, *Phys. Rev.*, **114**, 571 (1959).

²M. Bader, R. E. Pixley, F. S. Mozer, and W. Whaling, *Phys. Rev.*, **103**, 32 (1956).

³O. J. Runnalls and R. R. Boucher, *Can. J. Chem.*, **34**, 949 (1956).

⁴J. H. Roberts, MDDC-731 (1944).

⁵E. Segre and C. Wiegand, MDDC-185 (1944).

⁶H. L. Anderson, *Preliminary Report No. 3, Nuclear Science Series*, National Research Council, 1948.

ISOTOPE SEPARATION

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

HELIUM-3

Feed Gas Purification A charcoal trap is used in a system for purifying helium-3 prior to final enrichment by thermal diffusion. To determine the capacity of a new system, a 48-foot coil of 0.5-inch OD copper tubing containing 664 g activated charcoal was used to replace the present 28-foot coil. The 48-foot trap reduced the tritium content of helium-3 feed gas to 6.14×10^{-7} mole %. Traps to be installed in a new purification system will be similar to this one.

Vapor Pressure Thermometry Mound Laboratory is cooperating in an international effort to establish a helium-3 temperature scale in the range 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.

Weber and Schmidt⁷ fitted their data to the following equation for the thermomolecular pressure ratios of helium-4:

$$\begin{aligned} \log \frac{P_C}{P_W} = & \frac{1}{2} \log \frac{T_C}{T_W} - 0.18131 \log \frac{Y_C + 0.1878}{Y_W + 0.1878} \\ & + 0.41284 \log \frac{Y_C + 1.8311}{Y_W + 1.8311} \\ & + 0.15823 \log \frac{Y_C + 4.9930}{Y_W + 4.9930} \end{aligned}$$

where
$$y = \frac{273.15^\circ\text{K}}{T} - 1.147 \frac{R}{13.42}$$

The subscripts C and W refer to the cold and warm quantities, respectively; R denotes the tube radius in cm; P denotes pressure in microns of mercury; and T denotes temperature in $^\circ\text{K}$.

Each of the variables in the Weber-Schmidt equation was investigated to determine what effect could be ascribed to it. This study was made to provide a better understanding of the equation and to determine if there is sufficiently accurate and precise control and measurement of these variables in the experimental apparatus.

The first variable selected for investigation was the temperature at the warm end of the tube. This variable was discussed in a previous report.⁸ The effect of tube radius is discussed in this report, and the effect of cold temperature on helium gas not in equilibrium with its liquid will be discussed in a future report.

Figures 1 and 2 show the dependence of the differential pressure measured across the warm ends of tubes that are approximately 1/4 and 1/32 inch in diameter. It can be seen from Figure 1 that for tubes having a radius of approximately 0.025 cm, a change in radius of 0.01 cm will produce a maximum pressure deviation

⁷Leiden Comm. No. 246C (1936).

⁸Mound Laboratory Progress Report for March, 1964, MLM-1192.

of approximately 80 microns of mercury. Since the maximum total thermomolecular pressure being dealt with in the present experiments is of the order of 200 microns of mercury, the tube radius for small tubes is critical in accurate work.

In view of the above, it was necessary to determine as accurately as possible the ID of the 1/32-inch tube being used in the current experimental apparatus. The ID was measured microscopically at 100X magnification. Four diameter measurements were taken on each of five sections with the following results:

Section	Inside Radius (cm)
1	0.0251 $\pm$ 0.0002
2	0.0247 $\pm$ 0.0003
3	0.0247 $\pm$ 0.0005
4	0.0253 $\pm$ 0.0001
5	0.0250 $\pm$ 0.0001

For use in future calculations, the average value of 0.0249 ± 0.0006 cm will be used instead of the manufacturer's specified value of 0.0245 cm.

The largest deviation observed in all of the 20 measurements was less than ± 0.006 cm. Using Figures 1 and 2, it is seen that this deviation can produce a maximum uncertainty in the thermomolecular pressure measurements of about five microns of mercury which would represent, at most, about 2.5% error in the data. Therefore, the tube radius should not cause serious discrepancies in the experimental data, provided (1) the radius is measured as described above and (2) no tubing smaller than 1/32 inch is used.

Two experimental runs were made using helium-4 in both the inner bath and the vapor pressure bulb for the purpose of checking system modifications. Thermomolecular pressure data shown in Figure 3 were obtained for both saturated and unsaturated gas, but a low temperature leak developed during the second run and restricted the conditions under which such data could be taken. The leak, which was through a soft solder joint from the outer helium-4 bath into the inner dewar vacuum jacket, was apparently caused by thermal stress during temperature cycling between room and liquid helium temperatures.

As yet an unexplained discrepancy exists between the present data and the predictions of the Weber-Schmidt equation cited above. The present data are, however, in general agreement with previous thermomolecular pressure measurements made at Mound Laboratory.

Superfluid Experiment The superfluid properties of liquid helium-4 below the lambda point (2.17°K) are being used to enrich the helium-3 content in dilute mixtures of helium-3 in helium-4. The process is being developed to recover the helium-3 in the thermal diffusion process raffinate.

A technique was developed to prevent the helium-4 from returning through the superleak after a separation.⁹ Maximum separation was obtained by adjusting the heater input to a point just below the onset of boiling on the waste side of the superleak. The surrounding helium bath in the cryostat was then warmed slowly. The temperatures were monitored closely by mercury manometers, the important point being that the liquid in the waste chamber was kept warmer than both the bath and the input side of the leak. When the bath and the two reservoirs were above the lambda point, the warm-up was accelerated by introducing a small amount of helium into the cryostat vacuum jacket. After the warm-up was completed, the pressure across the superleak was equalized by pumping off the waste gas. The system was allowed to equilibrate for a day before product samples were taken.

⁹Mound Laboratory Progress Report for April, 1964, MLM-1196.

Figure 1. The Difference Between The Helium-4 Thermomolecular Pressure Gradients in Tubes With Approximately 1/4- and 1/32-inch OD as a Function of Inside Radius (Ambient Temperature 294°K).

Figure 2. The Difference Between the Thermomolecular Gradients (in Tubes With Approximately 1/4- and 1/32-inch OD) Per 0.01 cm Inside Radius as a Function of Cold Temperature for Helium-4 (Ambient Temperature 294°K).

Figure 3. Difference Between the Thermomolecular Pressures at the Warm Ends of Approximately 1/4- and 1/32-inch OD Tubes as a Function of Warm End Pressure in the 1/4-inch Tube.

A continuous process was simulated by heat flushing a quantity of the feed mixture, then making up the enriched product with more feed gas to the initial volume and flushing again. An overall enrichment of 38 was obtained in five passes. Results are given in Table 1. Helium-3 was detected in the raffinate only after the last run when the valves on either side of the leak were inadvertently left open for over a day before the sample was taken. Thus, over a relatively long period of time, some gas diffuses through the filter.

The product enrichment increases approximately linearly with the successive runs. Thus, an indication may be obtained as to how enrichment would progress in a continuous process. Since the flow of superfluid through the leak is very rapid, the rate of the process would be determined by the rate at which the sample could be condensed out and the raffinate removed.

Table 1

HELIUM-3 CONCENTRATION IN SUPERFLUID EXPERIMENTS

Feed (%)	Product (%)	Raffinate (%)	Enrichment Factor
0.08	0.81	0.00	10.1
0.14	1.42	0.00	10.1
0.17	2.20	0.00	12.9
0.29	2.41	0.00	8.3
0.39	3.05	0.16	7.8

ARGON ISOTOPE SEPARATION

Samples of gas were taken from the argon thermal diffusion system 33 days after it had been started up with natural abundance feed gas. Isotopic concentrations in Stages 3 and 4 were as follows:

	Argon-36 (mole %)	Argon-38 (mole %)	Argon-40 (mole %)
Top of 4th stage	99.55	0.39	0.05
Bottom of 4th stage	74.65	7.33	18.03
Bottom of 3rd stage	2.54	1.68	95.78

Line modifications are being made for argon-38 continuous draw-off at the bottom of either the third or fourth stage.

XENON ISOTOPE SEPARATION AND PURIFICATION

Thermal Diffusion The eight-column, five-stage, swing cascade thermal diffusion system was operated at 170 torr and about 850°C wire temperature to enrich xenon-136. Figure 4 shows the rate of change of the xenon-131 and -136 concentration in the swing reservoir at the bottom of the last stage. The gas at the bottom of the last stage reached the following isotopic concentrations in 29 days:

Isotope	Concentration (%)
xenon-131	0.55
xenon-132	1.96
xenon-134	15.79
xenon-136	81.71

Figure 4. Product Concentrations of Xenon-131 and -136 at Stage 5 Bottom of the Swing Cascade Thermal Diffusion System (Column Pressure = 170 mm; Wire Temperature = 850°C).

A light fraction from a previous xenon isotope separation had accumulated 2.66% krypton, which was removed by thermal diffusion and gas chromatography. A two-column cascade system operating at about one atmosphere pressure allowed removal of the krypton impurity at the top of the second stage. After the krypton concentration was reduced to 0.30%, the system pressure was lowered to 170 torr for xenon-131 enrichment. After several days of operation the second stage top concentration was 20.88% xenon-131.

Experimental Chromatograph The chromatograph was used to purify krypton-contaminated xenon, which had been separated by thermal diffusion (see above). The contaminants were 2.66% krypton, 0.02% argon, 0.55% nitrogen, 0.01% water, and 0.09% hydrogen. Nitrogen was used as the carrier gas. The column was operated at 193°K until the krypton peaked; then the temperature was raised to 243°K. The krypton trap was replaced by the xenon trap when the krypton peak returned to the baseline. The product was 99.81% xenon. The impurities were reduced to no detectable krypton, 0.05% hydrogen, 0.02% water, and 0.12% nitrogen. By nuclear counting the concentration of krypton-85 in the feed was $3.11 \times 10^{-5}\%$. The concentration in the product was $9.647 \times 10^{-8}\%$. This value represents a clean-up factor of 3220. The product was 61% of the gas processed, or 573 milliliters.

Xenon Tube Bundle A 24-column system for separating xenon isotopes by thermal diffusion is under construction. The cold wall tube is 0.568 inches ID, and the hot wall is the surface of a 0.315-inch OD tubular heater. The active length of the columns is 12 feet.

A prototype column was constructed for testing purposes. The column was operated with argon as a test gas. Static separation measurements were made at 3,500 and 2,500 torr with a hot wall temperature of 800°C and an average cold wall temperature of 25°C. The results, which are given in Table 2, are in reasonably good agreement with results predicted from the shape factors of McInteer and Reisfeld.¹⁰

¹⁰B. B. McInteer and M. J. Reisfeld, LAMS 2517, Feb. 1961.

Table 2

STATIC TESTS OF XENON TYPE BUNDLE COLUMN PROTOTYPE WITH ARGON

Pressure (torr)	Composition (%)				Log Separation Factor (ln q) Experimental	Theory
	Top		Bottom			
	Ar ³⁶	Ar ⁴⁰	Ar ³⁶	Ar ⁴⁰		
2500	39.88	59.22	0.01	99.96	8.9 + 7	11.0
3500	26.00	72.54	0.12	99.82	5.73	6.36

THERMAL DIFFUSION RESEARCH

Center Wire Heating by Alternating Current Experiments are being performed with alternating rather than direct current as the power source for heating center wires in thermal diffusion columns. One neon isotope separation run was made with a 24-foot column, a mercury well was used instead of the spring tension damping trap. The wire was heated to approximately 800°C in 30 seconds to avoid vibration. At 800°C there was no visible wire vibration during the 46-hour run. The neon samples from this run are being analyzed.

CARBON ISOTOPE SEPARATION

Thermal Diffusion Enriched methane was used as feed for the 11-column, 9-stage thermal diffusion cascade. Approximately 18 g of carbon-13 was accumulated in the form of methane. Isotopic purity of this product ranges from 90 to 94% carbon-13 in total carbon. The chemical purity of most of the methane is 95 to 98% with nitrogen as the major impurity.

Conversion of Enriched Methane to Barium Carbonate In order to supply carbon-13 in the form of barium carbonate, a system has been built to make the conversion from methane. Enriched methane is burned in oxygen over a heated platinum filament. The resulting carbon dioxide is absorbed in a barium hydroxide solution, and barium carbonate is precipitated. Test runs with natural abundance methane showed complete recovery of the carbon as barium carbonate.

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

Flexane-30, a two part polyurethane potting material (Devcon Corporation), was used as a base for the preparation of seven flexible conductive adhesives. Plug tensile strengths of the formulations were relatively low, 110-200 psi, but all formulations exhibited satisfactory low temperature flexibility and peel strength. The electrical resistivity was higher than desired; the lowest being four ohm-centimeters. The resistivity increased during aging.

Three silicone base adhesives, Sylgard 182, RTV-601 and Q9-0092 (Dow-Corning Corp.) were evaluated as matrices for conductive adhesives. When filled with silver powder, all formulations exhibited low peel strength. Three tackifiers, Indopol L-10, Indopol H-100 (Amco Chemical Corporation) and Koresin (General Aniline and Film Corporation) were added to LTV-602 - carbon black formulations to determine their effect on the peel strength of the cured adhesive. The addition of 5-30 weight % tackifier caused no improvement.

ANALYTICAL

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

LOW-LEVEL KRYPTON-85 COUNTING

It is the practice always to use new gas samples of krypton-in-xenon standards to calibrate the one-liter proportional counting chambers. A study was made to determine whether these gas samples could be used more than once as calibration standards. In this case Johnston internal gas phase proportional counters were used. The procedure employed was as follows:

1. Make a proportional counting gas by mixing methane with the krypton-in-xenon standard
2. Fill the one-liter chamber.
3. Determine the percentage of krypton-85 in the xenon
4. Return the mixture to the gas handling system
5. Freeze out the krypton-in-xenon and pump off the methane
6. Repeat Steps 1 through 3

The krypton-85 content in xenon was initially 2.4×10^{-9} atom %. Following Step 5 the krypton-85 content decreased to 1.2×10^{-11} atom %. Thus, it is not possible to use a given krypton-in-xenon standard more than once.

This study was expanded to include the krypton-in-xenon gas obtained by thermal diffusion at Mound Laboratory. Steps 1 through 6 were repeated with a sample of the gas. Step 5 is presented in detail as follows: In this study, (1) the mixture was frozen out in a cold finger; (2) the cold finger was valved off; (3) the residual gas was pumped off; (4) the gas in the cold finger was allowed to return to room temperature and expand back into the lines; (5) it was once again frozen out in the cold finger, and the procedure was repeated until a residual vapor pressure of approximately five torr was observed. Then, the entire Step 5 was repeated eight times. This procedure resulted in a reduction of the krypton-85 content from 1.6×10^{-9} to 3.3×10^{-10} atom % and resulted in a decrease in the krypton-xenon gas pressure of about 4.5%. Samples of the krypton-in-xenon were collected prior to and following these two studies. The results indicate that this technique may be a simple method for the removal of krypton-85 from xenon. These samples are to be analyzed to ascertain whether a change in the isotopic ratios resulted from this technique.

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.

ACTINIUM-227 SEPARATION

Actinium-227 on the tracer level was satisfactorily separated from its daughter products, radium-223, thorium-227, francium-223, radon-219, polonium-211 and -215, lead-207 and -211, and bismuth-211 using Dowex (AG) 50W-X8 ion exchange resin.¹¹

Actinium was eluted in the 4 *M* HNO₃ fraction. Alpha and beta counting of this fraction indicated that about 1.3% decayed by alpha emission and about 98.7% decayed by beta emission. The published figures for actinium decay are 1.2% by alpha radiation and 98.8% by beta radiation.

No more than trace quantities of thorium-227 were eluted by 4 *M* HNO₃. Complete separation would be impossible since the thorium-227 is a decay product of actinium-227 and will continually increase in this fraction until equilibrium is reached.

Rapid decay of the material in the 2 *M* HCl fraction indicated that it was composed almost entirely of 3.61-minute half-life lead-211, 216-minute bismuth-211, and 21-minute francium-223. The radium-223 was eluted in the 2 *M* HNO₃ fraction as expected. The radium, actinium, and thorium elution peaks were confirmed by alpha energy analysis.

URANIUM-234 SEPARATION AND PURIFICATION

Uranium-234 is being separated from aged plutonium-238 solutions and purified by a combination of anion exchange and solvent extraction techniques. A sample has been processed through the anion exchange step resulting in a solution which contains 1.94 g uranium (87% recovery) and 1.20 g plutonium (1.1% of original). A final purification step was applied to the uranium product 5HD, and cold work on solvent extraction behavior was continued.¹²

Conditions for anion exchange Run IV were generally the same as for previous runs except that fresh resin was used. The loaded column was washed with nearly six liters of HNO₃, then eluted with about three liters of dilute HNO₃. The analytical results and a summary of the run are given in Table 3. Overloading of the column, and the resulting plutonium breakthrough resulted in poor separation of plutonium from the uranium fraction (raffinates), but the uranium decontamination of the plutonium elutriates was excellent. Again the uranium mass balance showed a net gain, with the higher figure judged to be the more accurate.

Various waste solutions containing recoverable quantities of uranium were evaporated to approximately 900 ml (Solution S3-5A). After reduction with hydrazine and adjustment of the acid concentration, the solution contained about 16 g plutonium and nearly 2 g uranium. The solution was processed in Ion Exchange Run V. The column was washed with about six liters of wash solution and eluted with 3.4 liters of dilute HNO₃. The analytical results and a summary of the run are given in Table 4.

¹¹Mound Laboratory Progress Report for April, 1964, MLM-1196.

¹²See previous progress reports in this series.

Table 3

RESULTS OF ION EXCHANGE RUN IV

Solution	Vol. (ml)	Pu (g) ^a	U (mg) ^a	Comments
S3-4	910	36.16	548	Feed Solution
4R1	491	0.011	0	Column 90% loaded
4R2	978	3.41	387	Column completely loaded, some breakthrough
4R3	958	0.324	266	7.2 <u>N</u> HNO ₃ Wash
4R4	965	0.366	145	7.2 <u>N</u> HNO ₃ Wash
4R5	989	0.468	61	Backwashed Column
4R6	956	0.537	36	Wash; 7.2 <u>N</u> HNO ₃
4R7	<u>452</u>	<u>0.736</u>	<u>24</u>	Wash; 7.2 <u>N</u> HNO ₃
	5789	5.853	919	
4E1	360	10.04	48	First portion of elutriate
4E2-4 ^b	2900	<u>18.98</u>	<u>10</u>	Pu Elutriate
		34.87	977	

^aPu determined by alpha counting; U determined by modified PAN method.

^bSolution evaporated down before sampling and analyzing.

Table 4

RESULTS OF ION EXCHANGE RUN V

Solution	Vol. (ml)	Pu (g) ^a	U (mg) ^a	Comments
S3-5A	908	16.04	1978	Feed Solution; 7.2 <u>N</u> HNO ₃
5R1	925	0.012	0	Column 70% loaded
5R2	932	0.069	408	Column 75% loaded
5R3	941	0.222	696	7.2 <u>N</u> HNO ₃
5R4	938	0.182	385	Backwashed; some fresh resin at bottom.
5R5	932	0.181	244	7.2 <u>N</u> HNO ₃ Wash
5R6	940	0.150	132	7.2 <u>N</u> HNO ₃ Wash
5R7	901	0.133	50	~ 6 <u>N</u> HNO ₃ Wash
5R8	<u>581</u>	<u>0.250</u>	<u>22</u>	~ 2 <u>N</u> HNO ₃ Wash
	7090	1.199	1937	
5E1	102	0.838	0	First portion of elutriate
5E2-4 ^b	3400	<u>12.31</u>	<u>67</u>	Pu Elutriate
		14.347	2004	

^aPu determined by alpha counting; U determined by modified PAN method.

^bElutriates evaporated down with Elutriate 4E1. Analyses obtained by difference.

Data on the uranium-plutonium separation efficiency in the five ion exchange runs is presented in Table 5. The designation of the categories as raffinate, recycle, and eluate was somewhat arbitrary since many of the raffinates and one of the eluates were recycled; and one of the recycle fractions (from Run IV) was not recycled. In general, recycle solutions were those collected during the change from washing to elution.

It is interesting to note that in each run the total uranium found after processing was always higher than the initial value. This effect was most pronounced in Runs I and IV where the feed solution contained large quantities of impurities (from dissolution of part of the Haynes Alloy and stainless steel containers). Therefore, in calculating the distribution of uranium, the larger value was always used.

Table 5

PLUTONIUM-URANIUM SEPARATION EFFICIENCY

		Plutonium Concentration		Uranium Concentration	
		(g)	(%)	(g)	(%)
Run I	Feed	39.84	100	0.394	
	Raffinates	1.131	2.8	0.212	39.8
	Recycle	0.004	0.0	0.003	0.6
	Eluate	33.13	83.2	0.317	59.6
		34.265	86.0	0.532	100
Run II	Feed	33.13	100	0.317	
	Raffinates	0.545	1.6	0.194	50.4
	Recycle	5.62	17.0	0.038	9.9
	Eluate	31.93	96.4	0.153	39.7
		38.095	115	0.385	100
Run III	Feed	26.03	100	0.664	
	Raffinates	1.872	7.2	0.625	87.4
	Recycle	2.797	10.7	0.067	9.4
	Eluate	21.26	81.7	0.023	3.2
		25.93	99.6	0.715	100
Run IV	Feed	36.16	100	0.548	
	Raffinates	5.853	16.2	0.919	94.1
	Recycle	10.04	27.8	0.048	4.9
	Eluate	18.98	52.5	0.010	1.0
		34.87	96.4	0.977	100
Run V	Feed	16.04	100	1.978	
	Raffinate	1.20	7.5	1.937	96.7
	Recycle	0.84	5.2	0.000	0.0
	Eluate	12.31	76.7	0.067	3.3
		14.35	89.4	2.004	100

For plutonium, however, some losses occurred in the process and the initial analysis was used in the calculations. In the processing, primary emphasis was placed on separating the uranium from the plutonium, and the data show that uranium losses in the eluates ranged from a high of 60% down to 1%. The high uranium losses in the first two runs were caused by insufficient volumes of wash. In the last three runs, washes of 10-15 column volumes consistently gave uranium recoveries of 95% or better. The high plutonium concentrations in many of the raffinate solutions were due to overloading of the column, although incomplete reduction to tetravalent plutonium was probably also a factor.

An interesting sidelight appeared in the evaluation of Run IV. The uranium (977 mg) was 2.70% of the plutonium (36.16 g), while the overall average was 2.05% uranium (2.238 g) in plutonium (109.08 g). The difference is more striking when the values for Run IV are subtracted from the total, leaving 1.261 g uranium and 72.92 g plutonium for a uranium concentration of 1.73%.

The probable explanation for this separation lies in the prior history of the material. During the evaluation of this particular material, a hole was drilled through its double containers, and the entire assembly was heated to 900°C in a closed stainless steel container. During heating some of the plutonium metal spattered out of the capsule into the stainless steel container. Subsequent heating caused some corrosion of both the capsule and the stainless steel container. This spattered plutonium material was dissolved in 1:1 HCl, then converted to a HNO₃ medium and used as the feed solution for ion exchange Run IV.

The phase diagram of the uranium-plutonium system shows a eutectic point at about 10% uranium. It is plausible that during the storage of the material, a uranium concentration gradient was established. During the heating step, the high uranium fraction melted first and was forced out of the capsule by the pressure of helium gas (from alpha disintegration). Other impurities such as iron may have been present and contributed to the lowering of the melting point.

Impurities in the feed solution were analyzed by emission spectroscopy. The results showed gross amounts of iron, chromium, nickel, cobalt, aluminum and manganese, decreasing in that order. However, the corrosion and subsequent dissolution of parts of the capsule and the stainless steel container could easily account for these impurities, so no further conclusions could be drawn.

Uranium product 5HD from earlier processing was treated by an anion exchange procedure to remove additional impurities. The sample, containing over 70 mg uranium-234 in 10 ml $\underline{N}$ HNO₃, was used to dissolve 18 g Al(NO₃)₃/9H₂O; the resulting solution was diluted to 30 ml. This solution was calculated to be 1.6 molar in aluminum nitrate and 0.3 normal in nitric acid. The uranium was loaded on a 1-cm diameter, 6-cm high column of Dowex 1X4, which had previously been conditioned with the same aluminum nitrate solution. The column was washed with 1.6 $\underline{M}$ Al(NO₃)₃/0.3 $\underline{N}$ HNO₃ containing some ferrous ion (to reduce the plutonium to the nonadsorbed trivalent state), then with additional Al(NO₃)₃/HNO₃. The aluminum was washed from the column with 8 $\underline{N}$ HCl and finally the uranium was eluted with 0.1 $\underline{N}$ HCl. The eluate solution (designated 5HE) was evaporated to dryness, then taken up in $\underline{N}$ HNO₃, and evaporated to dryness two additional times before dilution to 10 ml with $\underline{N}$ HNO₃. Analytical results on samples taken before (5HD) and after (5HE) the purification are given in Table 6. The separation of aluminum and iron was good, but apparently little of the plutonium was removed.

Cold work on the tributyl phosphate (TBP) solvent extraction system was continued from last month. In a study of reagents to strip the uranium from the organic phase, urea and oxalic acid solutions proved to be unsatisfactory because precipitates were formed. Nor did acetic acid strip the uranium. Various concentrations of sodium carbonate and two concentrations of hydroxylamine hydrochloride were examined and the results are shown in Table 7. Sodium carbonate at a concentration of 2% or higher was an excellent stripping agent. But hydroxylamine stripped only a relatively small amount of uranium. Since hydroxylamine reduces plutonium to the nonextractable trivalent oxidation state, it is possible to selectively strip the plutonium leaving the bulk of the uranium in the organic phase.

Table 6

PURIFICATION AND CHARACTERIZATION OF 5H URANIUM PRODUCT

	5HD	5HE
Total alpha count (d/min.)	2.22×10^9	1.89×10^9
Count due to U-234 (%)	46.9	51.9
Calc. U-234 (mg)	76.2	71.8
Calc. Pu (mg)	0.0065	0.0024
Uranium Analysis	78 (single)	72 (triplicate)
Impurities (by emission spectroscopy)		
Aluminum (mg)	120	nil
Copper (mg)	<4	<4
Iron (mg)	4	trace
Silicon (mg)	<20	<20
U ²³⁴ by Mass Spectrometry (%)		98+

Table 7

STRIPPING URANIUM FROM TRIBUTYL PHOSPHATE

Stripping Solution	Percentage Stripped
Deionized water	77.5
0.1% sodium carbonate	74.6
0.5% sodium carbonate	54.3
1.0% sodium carbonate	53.0
2.0% sodium carbonate	100
3.0% sodium carbonate	100
2 <u>M</u> NH ₂ OH-HCl/1 <u>N</u> HNO ₃	8.7
4 <u>M</u> NH ₂ OH-HCl/2 <u>N</u> HNO ₃	4.5

Conditions: Equal volumes of organic and aqueous solutions were shaken for six minutes. Uranium analyses by Modified PAN Method.