MLM-1157
TID-4500 (24th Ed.)
Category - UC-2
Progress Reports

MOUND LABORATORY PROGRESS REPORT FOR MAY, 1963

J. F. Eichelberger
G. R. Grove
L. V. Jones
E. A. Rembold

Date: May 31, 1963

The Mound Laboratory Progress Report, issued monthly, 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 month, 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-1145
MLM-1146
MLM-1148
MLM-1151
MLM-1152
MLM-1155

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO CHEMICAL COMPANY

MOUND LABORATORY

MIAMISBURG, OHIO

OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

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

This document is
PUBLICLY RELEASABLE
Hugh Kinser
Authorizing Official
Date: 5/26/09

DISCLAIMER

TABLE OF CONTENTS

Adhesives and Plastics Research

Radioelements Research

Isotope Separation

Alpha and Neutron Source Development

Analytical

SUMMARY

Adhesives and Plastics Research

Adhesives Two flexible adhesives and a rigid silver-filled epoxy adhesive were used to study the effects of temperature and aging on the electrical resistivity of conductive adhesives. After heating there was usually a decrease in resistivity; however, due to possible unintentional strain on the adhesive bond, definite conclusions could not be drawn.

Radioelements Research

Polonium The alpha/gamma counting ratio of the polonium-208 sample recently returned from Argonne National Laboratory was $(3.15 \pm 0.15) \times 10^3$.

Tellurium was found to be present in purified polonium-208. A precipitation of ferric hydroxide carried appreciable amounts of tellurium as well as polonium; but when the ferric hydroxide was precipitated with ammonia in the presence of nickel, the amount of tellurium carried was reduced.

Polonium process waste solutions were effectively decontaminated with a second precipitation of ferric hydroxide. The pH of the solution should be low enough for complete dissolution of iron, before the precipitation is carried out.

Extensive half-life studies are being made on a small polonium-208-polonium-209 sample. The half-life of polonium-208 is between 1052.4 and 1058.0 days, and the half-life of polonium-209 is between 13 and 100 years. Another isotope may have been present in the original sample.

Residue Adsorption Anomalous results in the desorption of radium-223, barium-140, and strontium-90 from hydroxide residues were traced to the three normal ammonium hydroxide used for these experiments. When fresh ammonium hydroxide solution was used, the strontium-90 hydroxide was quantitatively desorbed by distilled water, leaving yttrium-90 quantitatively adsorbed. It is expected that when the experiments with barium-140 and radium-223 are repeated, these radioelements will separate quantitatively from lanthanum-140 and actinium-227, respectively.

Isotope Separation

Carbon-13 Mound Laboratory is preparing gram quantities of greater than 90 per cent carbon-13 using methane or carbon monoxide as feed. Various thermal diffusion column configurations are being evaluated.

The first four stages of the seven-stage cascade system of hot-wire and concentric-tube columns were started to enrich natural methane to about 90 per cent carbon-13. The concentric tube columns have concentrated enriched feed methane from 60 per cent to over 90 per cent carbon-13 in the total carbon. About 1.5 grams of a product containing about 10 per cent impurities has been accumulated.

The use of alternating current for heating in a hot-wire thermal diffusion column is being studied. The addition of weight to a suspended wire has an insignificant effect on wire vibration. Wire length had a varying effect on vibration and will be a design factor if alternating current is used in thermal diffusion. Wire material was also studied; in the 321 stainless steel and Nichrome V wires there was no visible vibration above 25 amperes.

Xenon In two chromatographic runs with 500-cubic centimeter feed samples, separation factors of 904 and 1,186 were obtained. The adsorbent was 6/14 mesh Columbia AC-grade carbon.

Thermal Diffusion Theory A second order differential equation was developed for deriving the convective velocity in a thermal diffusion column. Although the equation must be solved numerically, the functional dependence of the velocity on the column geometry can be determined easily.

Alpha and Neutron Source Development

Neutron Measurements In determining the error due to deviation from point-source geometry, it was assumed that the error introduced by ignoring neutron scattering within a source would be negligible. Further analysis has shown that the error may not be negligible; therefore, it is presently being evaluated.

Analytical

Krypton-85 The method of analyzing krypton-85 in xenon by gamma counting was modified. The integrated gamma counting rate in the krypton-85 photopeak was compared to the krypton-85 concentration determined by internal gas counting to obtain a calibration factor for the gamma counting rate.

A low-level counting system was assembled for precise measurement of very low levels (about 10^{-15} per cent) of krypton-85 in xenon. High background counting rates were attributed to slight contamination of the gas handling system and natural radioactivity in the lead shielding. The detectability of the present system is approximately 10^{-13} atom per cent krypton-85.

ADHESIVES AND PLASTICS RESEARCH

Adhesive formulations are being developed which are compatible with explosives. The cured formulation must be flexible at low temperatures, and it must retain its tensile strength at high temperatures. In addition, the properties of diallyl phthalate formulations are being evaluated to help produce superior plastic parts.

Adhesives

A preliminary study was made to determine the effect of aging, temperature, and mechanical stress on the electrical resistivity of conductive adhesives. Two flexible conductive adhesives and a rigid silver-filled epoxy adhesive were selected for this study.

Initial measurements on all specimens were made after an overnight cure at room temperature. Subsequent measurements were made at intervals after aging under varying conditions. After a heating period each specimen was conditioned at room temperature for three hours prior to the resistivity measurement.

It was found that even a slight stress on the flexible bond had a measurable effect on the observed resistivity, usually in the negative direction. This phenomenon was not exhibited by the rigid conductive epoxy adhesive at room temperature. Since mechanical stress affected the electrical resistivity of flexible conductive adhesives significantly, the decrease recorded was not wholly a result of aging and heating. Unintentional strain and stress on the bond, particularly during the heating periods, may have caused the change. In consideration of possible interrelated aging temperature stress-strain factors, no definite conclusions can be drawn from the study.

RADIOELEMENTS RESEARCH

Basic and applied research on a number of radioelements is being conducted to determine the 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.

Polonium

Polonium-208 and Polonium-209 in Irradiated Bismuth Since gamma rays are emitted in the decay of polonium-209 and, to a lesser extent, in the decay of polonium-208, an empirical value was determined for the alpha/gamma counting ratio in the Argonne polonium-208 returned from Argonne National Laboratory. Two sources approximately 0.2 microcurie each were prepared by spontaneous electrodeposition on silver. The silver plates were counted at 2π geometry in a gas flow proportional counter, and then on top of a three-inch by three-inch NaI(T1) scintillation crystal. The counting ratio (alpha/gamma) was found to be $(3.15 \pm 0.15) \times 10^3$. This ratio permitted the calculation of activity levels from gamma counting, a simpler method than alpha counting, especially if the sample contained large amounts of dissolved material.

Small amounts of tellurium were found in polonium purified by coprecipitation with tellurium and separated by ferric hydroxide precipitation and cation exchange resin chromatography. Apparently, the ferric hydroxide carried small amounts of tellurium in addition to nearly quantitatively removing the polonium. Normally, tellurium is completely soluble in ammonia, the precipitating agent used for ferric hydroxide. The amount of tellurium carried was reduced when the polonium (and tellurium) were deposited on nickel powder; the nickel powder was subsequently isolated when the polonium was carried on ferric hydroxide. The nickel remained in solution as an ammonia complex. Tellurium solubility seemed to increase by the presence of the soluble nickel complex. Polonium may be separated from the ferric ion by cation exchange resin chromatography. On the basis of the work performed thus far, the best procedure is to avoid using tellurium and to depend on the cation exchange resin to separate the polonium from nickel and iron.

Polonium Process Waste Disposal Further laboratory tests on the decontamination of polonium process wastes have been made. A second precipitation of ferric hydroxide showed that the amount of ferric sulfate added to the waste solution may be as little as 15 pounds. It was important that the pH of the solution be low enough after the addition of the ferric sulfate to dissolve all the ferric sulfate. The addition of 25 to 50 pounds of ferric sulfate automatically lowered the pH sufficiently, but with lesser amounts, acid (such as HCl) had to be added. When the ferric sulfate was completely dissolved, a more effective scavenging of the solution occurred as the ferric hydroxide precipitated.

Polonium-208-Polonium-209 Half-life Sample In February, 1952, a one-curie sample of polonium-208-polonium-209 was prepared for a calorimetric half-life determination of polonium-208. At the time, it was stated:

> All polonium-208 on hand (two curies) has been repurified and combined in one solution. Microfoils plated from this solution have a mass purity of 77 per cent as polonium-208, the other 23 per cent supposedly being polonium-209, polonium-210, and impurities. This material will be used for half-life determinations by calorimetry and counting, band spectral measurements, alpha-ray spectrograph, mass spectrograph and pulse height analyzer studies.[1]

The polonium-208 was produced by 19.2-Mev protons on bismuth-209. Band spectral measurements were later reported by Hunt and Pish as 15.5 ± per cent polonium-209 by weight.[2] Alpha pulse height analyses were performed by Asaro, who gave an alpha ratio of polonium-209 to polonium-208 of 0.0050 ± 0.0002.[3] A half-life of 103 years calculated from these two measurements (assuming 2.93 years for the half-life of polonium-208) is the currently accepted value. Kelly had estimated that the half-life was between 50 and 200 years.[4]

---

[1] MLM-670.

[2] MLM-735.

[3] F. Asaro, *Phys. Rev.*, **101**, 649 (1956).

[4] Kelly, Thesis, UCRL-1044, 1950.

The calorimeter sample was plated on three platinum foils and placed in a tantalum can (OD, 0.188 in.; height, 0.7 in.). The tantalum container was hermetically soldered into a brass container, which was sealed with a screw cap and a soft metal washer inside an aluminum container (OD, 0.281 in.; length, 0.90 in.). There has been no indication of spurious heating effects, corrosion, or measurable leakage of activity.

The gamma-ray spectrum of the sample was reported by Fox as Sample 1.[1] He measured the gross gamma-ray half-life as 7.4 ± 0.7 years. This value is reasonable since the source has three gamma rays: the 0.58-Mev gamma of polonium-208 (2.9 yrs) and the 0.255- and 0.900-Mev gamma rays of polonium-209 (12-100 yrs). A recent gamma-ray spectrum showed the 0.58-Mev peak slightly above background, whereas the 0.90- and 0.255-Mev peaks of polonium-209 were in approximately the same proportion as ten years ago. The gamma-ray spectrum of the source and the estimated magnitudes in microcuries were reported by Dagget and Grove.[2]

A two-curie polonium-208-beryllium neutron source was prepared at Mound Laboratory in March, 1953. The neutron level was followed by M. L. Randolph and co-workers at Oak Ridge National Laboratory. Their neutron half-life results were compared to Mound Laboratory preliminary results (1058 ± 1 days) for polonium-208 (obtained by assuming 100 years for polonium-209). Their value of 1041 ± 6 days indicated a possible overcorrection for polonium-209. The samples tested at Mound Laboratory and Oak Ridge National Laboratory came from different production batches.

Results of recent half-life calculations indicate that the measurements should be continued for at least another year to reduce the probable error in the half-life of polonium-209 as obtained from the calorimeter data alone. The source would then be opened, and the alpha activity ratio of the two isotopes would be measured to further improve the half-life value of polonium-209.

Table 1 gives the results of the half-life calculations of data from October 7, 1953, to October 2, 1962. The half-life of polonium-209 was varied, and the most probable values of the other constants were determined by the variational method.[3] The minimum sum of the deviations squared, Column 5, corresponds to 13.05 years for the half-life of polonium-209. The probable error per single observation (*P.E.S.O.*) is:

$$P.E.S.O. = 0.6745 \sqrt{\frac{184.94}{49-4}} = 1.37 \text{ microwatts}$$

Table 1

HALF-LIFE OF Po^{208} AND Po^{209} FROM 49 DATA POINTS TAKEN BETWEEN OCTOBER 7, 1953, AND OCTOBER 2, 1962

Assumed Half-life of Po^{209} (yrs)	Most Probable Half-life of Po^{208} (days)	Most Probable Initial Power of Po^{208} (microwatts)	Most Probable Initial Power of Po^{208} (microwatts)	Sum of Deviation Squared (microwatts)	Probable Error in $T_{1/2}$ Po^{208} (days)
197	1057.68	21,488.87	148.57	233.665	0.1770
120	1057.49	21,484.48	153.12	229.112	0.1767
100	1057.39	21,482.18	155.51	227.010	0.1768
80	1057.24	21,478.64	159.17	223.951	0.1768
61.86	1057.01	21,473.28	164.71	219.732	0.1771
14.7	1053.19	21,366.15	274.38	185.638	0.1924
13.05[a]	1052.38	21,340.39	300.66	184.937	0.1990
11.1	1051.10	21,294.74	346.87	186.713	0.2094

[a] Most probable half-life of Po^{209}.

---

[1] MLM-896.

[2] Dagget and Grove, *Phys. Rev.*, 99, 1 (1955).

[3] MLM-1148; MLM-1151.

By the following equation, reported earlier, the value of 13.04 years is 4.75 probable errors below 100 years:[1]

$$B = \frac{1}{P.E.S.O.}\sqrt{\sum d_i^2 \ (100 \text{ yrs}) - \sum d_i^2 \ (13.04 \text{ yrs})}$$

$$= \frac{1}{1.37}\sqrt{227.01 - 184.94} = 4.75$$

Previous experience has shown that calorimeter results seldom deviate more than three probable errors, although a deviational five probable errors has occurred.

From the two half-life determinations and the initial power of the two isotopes as indicated in Table 1, the mass percentage and alpha percentage of polonium-209 were calculated (Table 2). When 100 years is assumed for the half-life of polonium-209, the percentages are equal to those Hunt and Pish and Asaro obtained. A polonium-209 half-life of 13 years would cause an error factor of three in the determination of Hunt and Pish, and an error factor of two in Asaro's determination. At present, it seems more probable that the calorimeter is in error. There is also some indication that the calorimetric half-life of polonium-209 may increase with time.

Table 2

MASS AND ALPHA ACTIVITY PERCENTAGES OF POLONIUM-209

Assumed Half-life of Po^{209}	Po^{209} in Sample, by Mass (%)	Po^{209} in Sample, by Alpha Activity (%)
197	25.37	0.497
120	17.65	0.514
100	15.38	0.523
80	12.98	0.537
61.9	10.71	0.558
14.7	4.82	0.983
13.05	4.74	1.087
11.1	4.74	1.272

Ten additional measurements taken in April, 1963, were added to the calculations and three points were deleted, two with large deviations and one taken 316 days before any of the others. The resulting half-life for polonium-209 was 16.47 years, which is 5.35 probable errors below 100 years. The corresponding half-life for polonium-208 was 1053.95 days.

Even more confusing than the polonium-209 half-life is the short half-life appearing in the early data. Kelly, after investigating alpha activity produced by proton bombardment of bismuth-209, stated:

> . . . polonium-210 activity was found in an amount comparable to the polonium-209 activity. This corresponded to a cross section of nearly a millibarn at the peak of the polonium-210 curve and seemed rather too high for a (p, γ) reaction in competition with a (p, n) reaction. However, further investigation . . . indicated that essentially all of the polonium-210 must have been produced by the (p, γ) reaction.[2]

---

[1] MLM-1148.

[2] UCRL-1044.

A half-life sample of polonium-208 was followed by parallel-plate counting at Mound, and after 263 days a gross half-life of 1010 ± 14 days was calculated. At 400 days the observation was made:

> The half-life value is gradually increasing. However, an analysis of the results indicates a six per cent polonium-210 component. Since pulse-height analysis gave only a 0.5 per cent polonium-210 component, it seems evident that not much reliance can be placed on these data.[1]

The half-life sample, which was of older material at the initial measurements, gave a gross half-life initially of 1042 days. Another sample assayed for 46 days gave a gross half-life of 1038 days. When the early data were analyzed, assuming the half-life of polonium-210 (138.38 days), a good fit to the data was not obtained. When the data obtained with Calorimeter 51 were solved for the half-lives of polonium-208 and an unknown (while assuming a half-life and activity for polonium-209 given in Table 1), the corresponding value was obtained for the half-life of polonium-208 (Table 1). A half-life of 57.5 or 60.8 days was obtained for the unknown depending on whether 13.05 or 100 years was assumed as the half-life of polonium-209. The fit to the data was good, and the half-lives were less than that of polonium-210 by 4.9 probable errors. The result was a shorter half-life than polonium-210 by 1.0 and 0.5 probable errors, respectively, using Calorimeters 44 and 39. These results, however, do not prove that the short half-life material was not polonium-210; but they do explain the unusual amount of polonium-210 found by Kelly. These results also explain the counting half-life results and definitely decrease the deviations in calorimeter results.

In conclusion, the only definite statements that can be made about the polonium-208-polonium-209 half-life sample are: (1) the half-life of polonium-208 is between 1052.4 and 1058.0 days; (2) the half-life of polonium-209 is between 13 and 100 years; and (3) the activity thought to be polonium-210 may be another isotope of polonium with a half-life of approximately 60 days. The reliability in the half-lives of polonium-208 and polonium-209 will improve with time. Since the unknown isotope has completely decayed, little more will be learned without fresh samples, although further analysis of the calorimetry and counting data may clarify the problem of the half-life of polonium isotopes in this sample.

Residue Adsorption

In last month's report, a preliminary attempt at the sequential separation of protactinium, actinium, thorium, and radium by residue adsorption was described. The procedure consisted of depositing protactinium fluoride mixed with actinium, thorium, and radium nitrates on a gold surface. The deposit was dried, and the residue was converted to hydroxides, which were then leached successively with water, dilute nitric acid, and dilute hydrofluoric acid.

The separation was only partially successful. Specifically, the radium-223 was not desorbed quantitatively with distilled water, and it was necessary to use dilute nitric acid, which also desorbed part of the actinium; a portion of the thorium-227 was also desorbed with the protactinium-231 in dilute hydrofluoric acid.

The anomalous behavior of the radium-223 hydroxide with respect to its low desorption with water was investigated with an actinium equilibrium mixture free of protactinium:

Six stainless steel disks were cleaned and masked with methyl methacrylate in the usual manner, and a sample of the actinium equilibrium mixture (AEM) in dilute HNO_3 was mounted on one of them. The solution was dried at 90°C, and the residue was covered with 1/4 ml of 3$\underline{N}$ NH_4OH, dried, covered with 1/2 ml of water, dried, and heated for an additional five minutes at 90°C. The residue was leached successively with two 1/2-ml portions of water and several concentrations of HNO_3, ranging from 10^{-4} to 10^{-1} N. Each portion of leaching agent applied to the residue was heated for two minutes at 90°C before being transferred to another stainless steel disk. All the fractions were dried at 90°C, and the residues were covered with 0.1 $\underline{N}$

---

[1] *Ibid.*

HNO_3. One drop of concentrated NH_4OH was added to each solution, and the solutions were evaporated to dryness. The small residues of NH_4NO_3 were vaporized at 400°C, and the disks were ignited at red heat. The fractions were alpha-counted periodically for eight days, and the distribution of the three principal radioisotopes was determined by the method of differential decay.

The results (Table 3) again showed the failure of radium-223 to be desorbed by water from the hydroxide residue. Even in 10^{-4} normal nitric acid, the desorption was not complete. This behavior was unusual in view of the established behavior of strontium-90 under similar conditions.

Table 3

FRACTIONATION OF ACTINIUM-227, THORIUM-227, AND RADIUM-223 ON DESORPTION FROM STAINLESS STEEL

HNO_3 Normality	Amount Transferred (%)		
	Ac^{227}	Th^{227}	Ra^{223}
0.00 (OH^-)[a]	0.0	0.5	22.6
0.0001	9.2	0.0	48.9
0.001	71.8	1.0	17.8
0.01	9.9	61.2	4.0
0.1	2.5	27.4	2.4
Total Transferred	93.4	90.1	95.7
Residual	2.1	9.4	4.1
Material Balance	95.5	99.5	99.8

[a] Hydroxide residue leached with distilled water.

To test the possibility that interference with the radium-223 desorption was caused by some impurity in the original AEM, a sample of AEM was evaporated to dryness in a glass vial; the residue was leached successively with three normal ammonium hydroxide, water, and several concentrations of nitric acid. The gamma spectra of the ammonium hydroxide and water fractions showed that they contained radiochemically pure radium-223. The 10^{-4} and 10^{-3} normal nitric acid fractions contained, by alpha spectrometry, nearly all of the actinium-227 with some radium-223; the 10^{-2} normal nitric acid fractions contained, by alpha spectrometry, nearly all of the actinium-227 with some radium-223; the 10^{-2} normal nitric acid contained nearly pure thorium-227, as did the original vial. All fractions were evaporated to dryness, and their residues were taken up in normal nitric acid.

The two radium-223 fractions were tested for desorption from a hydroxide residue with poor results; there was slightly more desorption of the radium-223, which had originally been leached with water, as compared with that leached with three normal ammonium hydroxide (44.8% as compared with 36.0%).

The thorium-227 fractions were allowed to decay to radium-223 for five days; then they were combined and sampled. The sample was converted to the hydroxide form and leached with distilled water. The alpha spectrum showed again that the radium-223 was not quantitatively separated. These results indicated that an impurity in the AEM could not be causing the failure of the radium-223 to desorb since the thorium-227 fractions should have been nearly free of that impurity after the extensive leaching.

As an alternate hypothesis the difference in the specific activities of radium-223 and strontium-90 was considered. The strontium-90 separations had been made in the nanogram range while the radium-223 was in the picogram range. If the difference in behavior were due to the relative quantities of the two radioelements, the addition of carrier to the radium-223 should make them behave similarly. Instead of radium-223, ($T_{1/2}$ = 11.4 days) samples of barium-140 ($T_{1/2}$ = 12.8 days) were used to test the effect of added carrier. A series of experiments was carried out in which quantities of barium carrier, ranging from one nanogram to one microgram, were added to the barium-140. Even with one microgram of barium carrier, only about half of the barium-140 was desorbed. With no carrier added, less than 40 per cent of the barium-140 was desorbed.

As a test of the reagents, a sample of carrier-free strontium-90 was mounted, and the desorption procedure was carried out in the identical manner. When only 30 per cent of the strontium-90 was desorbed, it became evident that a trace impurity in one of the reagents was responsible for the anomalous results. The impurity was located in the ammonium hydroxide; the experiment was repeated; and the strontium-90 was quantitatively separated.

The experiments with radium-223 and barium-140 have yet to be repeated, but it seems certain that the impurity has now been isolated, although not identified. It seems probable that the unknown impurity has one of two sources; atmospheric carbon dioxide or the rubber bulb used with the ammonium hydroxide dropper bottle.

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.

Carbon-13

Thermal Diffusion The objectives of the carbon-13 research program are the preparation of 90 per cent purity carbon-13, the evaluation of carbon monoxide and methane as feed materials, and the evaluation of various separation methods.

A three-column system is being used for enrichment of natural methane. At the bottom of the third stage the carbon-13 content is eight per cent in 71 per cent methane at a flow rate of one milliliter per hour.

A six-column, four-stage cascade is being used for partial enrichment of mass 17 methane. Gas has been fed through the stripping section of the cascade at a rate of 30 to 35 liters (STP) per day since April 11. No withdrawals were made from the bottom. By May 3, the composition in the bottom reservoir (about 1.5 liters capacity) had risen to 7.8 per cent mass 17 in 56 per cent total methane.

The magnitude of the initial transport of carbon-13 into the column system is approximately half the value expected on the basis of single column performance. This discrepancy is thought to be the result of pressure excursions and flow disturbances arising from operation of one or more of the components of the feed, draw-off, and circulating systems.

Methane Purification Analytical results for Run 28 on the methane purification system showed that the methane was upgraded from 99.0 to 99.8 per cent. The product quantity was 16.6 STP liters. In this run, two-thirds of the methane charge was boiled off as raffinate. While this increase from one third to two thirds high vapor pressure material boil-off has not greatly increased the total methane purity, neither carbon monoxide nor nitrogen appeared in the product. The product from the one third boil-off previously contained these two impurities.

Simplified Methane Feed Purification A simplified procedure has been set up for partial purification of methane used to feed the thermal diffusion column system. Volatile impurities are removed by pumping at liquid nitrogen temperature on batches of 400 to 800 liters (STP). Heavy impurities are removed in a six-foot long, two-inch inside diameter adsorption column. The column is packed with activated charcoal and Linde 5A molecular sieve, and it is inserted in the feed line to the thermal diffusion system. A second identical column is available for alternate use during regeneration of the absorbent. The absorbent is regenerated by vacuum pumping and heating. Feed material of 99.6 to 99.7 per cent purity is routinely obtained from tank gas of 99.0 per cent or less.

Chemical Exchange The two most promising methods for the enrichment of carbon-13 by chemical exchange, the cyanide method and the bicarbonate method, were studied in great detail. Three reports on the cyanide method were based on the same chemical exchange reaction: $NaCN \rightarrow HCN$. The most efficient production of carbon-13 using the cyanide method was that achieved by E. W. Becker and co-workers, who used a four-stage cascade capable of producing 0.25 gram of carbon-13 in a concentration of 12 per cent.[1] The equilibrium time required was 53 hours. Each of the four columns was 2.6 meters long, or a total of 10.4 meters. There were also included in the system two additional stripping columns, each 2.6 meters long. The other two reports on the cyanide method were similar to that of Becker's and demonstrated, in general, less efficient separation.

---

[1] Becker, *Z. Naturforsch*, 7a, 664 (1952).

Four reports on the bicarbonate method included the classic study made by Urey.[1] He proposed a large plant capable of producing 1.46 grams of carbon-13 per day in a concentration of 33 per cent. The plant utilized a total column length of 512 feet and required 87 days to reach equilibrium. In one Russian report, a separation of 1.046 was achieved in a two-meter column using a heterogeneous aluminum silicate catalyst. In another Russian report, an aqueous solution of monoethanolamine was used. The reaction was catalyzed by the use of the enzyme carbonic anhydrase. A six-meter column was used, but equilibrium was reached in 20 hours. A carbon-13 separation at 1.09 was estimated indirectly. In the fourth report on the bicarbonate method monoethanolamine was used in a nonaqueous solution of methanol. In a column 1.96 meters long, separations of 1.15 to 1.38 were obtained, depending on the flow rates and temperature.

The last report appears to be the most promising for the bicarbonate method. Although its rate of production is lower than that described by Urey, 18 atmospheres operating pressure were required to achieve Urey's results. On the other hand, the nonaqueous monoethanolamine method would be preferable if its reaction rate could be increased, because the separation in this reaction is dependent on the reaction rate and not on the diffusion rate of the carbon dioxide. Likewise, the reaction rate may be increased by using a different solvent as catalyst, by increasing pressure, and by increasing temperature.

The overall column sizes, the enrichments, and the throughputs of the bicarbonate method and the cyanide method systems were compared. The results of this comparison showed that the cyanide method would produce more carbon-13 at a given enrichment than the bicarbonate method in a similar system. The comparisons were semiquantitatively made because systems of varying column size differ inherently in their efficiencies, i.e., those systems with the longer column lengths give more favorable results per foot than those which are shorter.

However, the cyanide method did not appear suitable for further development. Its reaction rate is controlled by the diffusion rate of the hydrogen cyanide; therefore, the column operates more efficiently at pressures lower than one atmosphere. Polymerization also is a particular disadvantage for large operations since column cleanup requires production shutdown. An advantage of the monoethanolamine method is simplicity in refluxing at the lower end of the column. This refluxing can be achieved merely by the use of a heater wherein the carbon dioxide is regenerated. Therefore, the monoethanolamine and carbon dioxide exchange appears more favorable from a development view point. In addition, its ease of operation and inherent simplicity make it especially attractive.

Electrical Heating Studies The use of alternating current to heat the center wire in hot-wire thermal diffusion columns is being studied. The wire was 1/16-inch diameter Nichrome V hung vertically in air. At the bottom an attached weight extended into a pool of mercury. Electrical leads (220 volts) were attached at the top of the wire and were placed in the pool of mercury. There was no horizontal support along the 12-foot length of wire.

The effect of increased weights on the vibration[2] of the wire was studied. The amplitude and length of the waves formed in the wire varied with the attached weight. The vibration could not be eliminated by addition of weight at currents below 25 amperes (approximately 705°C). Increasing the weight increased the wire length, and the increase may have caused the vibrations at 25 amperes when 2484 grams of weight were added. In general, the addition of weight to the wire had only a small effect on the vibration of the wire.

The effect of changes in wire length on the wire vibrations was studied. The data were obtained at 25 amperes of current, or a wire temperature of about 705°C. The data in Table 4 show that at various lengths the wire vibrates or comes into resonance. These data were obtained with 463 grams attached to the wire. If the wire is used for a thermal diffusion column with alternating current, the length of the wire must be carefully chosen to prevent vibration at elevated temperatures.

---

[1] Reid and Urey, *J. Chem. Phys.*, **11**, 403 (1943).

[2] Under certain circumstances the wire vibrated as the current was applied; see MLM-1155.

Table 4

THE EFFECT OF NICHROME V WIRE LENGTH ON WIRE VIBRATION

Cold Wire Length (cm)	Wire Length at 25 amps, ~705°C (cm)	Vibration One-Half Wave Length (in.)	Vibration Amplitude (in.)
363.60	367.63	No visible vibration	
361.34	365.47	No visible vibration	
358.91	363.00	No visible vibration	
356.30	360.33	No visible vibration	
353.79	357.75	Undefined	<1/32
351.13	355.11	8	<1/32
348.67	352.53	8	$\overline{<}$1/32
346.09	350.00	8	1/64
343.53	347.43	No visible vibration	
340.98	344.80	No visible vibration	
338.35	342.20	No visible vibration	
335.68	339.52	No visible vibration	
333.05	336.83	No visible vibration	
330.54	334.36	No visible vibration	
327.80	331.56	8	1/64
325.34	329.05	10	1/64
322.76	326.50	10	1/64
320.22	323.86	No visible vibration	
317.68	321.28	No visible vibration	
315.09	318.65	No visible vibration	
312.57	316.13	No visible vibration	
310.08	313.60	No visible vibration	
307.49	311.02	No visible vibration	

The effect of wire material on vibration was determined. The data are shown in Table 5. The data were run with 463 grams attached to the bottom of the 12-foot, 1/16 inch wires, and the data showed that at lower amperages and the resultant cooler temperatures the wire vibrations for iron wires were different from those for 321 stainless steel wires. The magnetism of both materials probably affected the vibration. When the amperage and temperature reached a certain point, the vibrations either stopped or the amplitude was reduced considerably; in most cases the vibration stopped in all but one plane perpendicular to the wire. As the amperage and temperature continued to increase, the vibration ceased. Vibrations stopped completely in only the iron wire; faint vibrations were determined by holding a piece of wood against the wire. The other wires had a slight vibration which was not visible but which was similar to a transformer hum.

Table 5

VIBRATIONS IN WIRES OF DIFFERENT MATERIALS

Material	Current (amp)	Temperature (°C)	One-Half Wave Length (in.)	Amplitude (in.)	Point Vibration Stopped Current (amp)	Point Vibration Stopped Temperature (°C)
Soft Iron[a]	10	60	Undefined	<1/64	Between 29.5-30.0	Between 632-790
	15	135	10-11	<1/64		
	20	230	10	<1/64-1/16		
	25	430	17	<1/64-1/16		
	30	790	No visible vibration			
Stainless Steel Number 321 (Magnetic)	10	180	12	<1/32	Between 22.0-22.5	Between 560-575
	15	350	12-13	<1/32		
	20	500	16	<1/32		
	25	642	No visible vibration			
	30	760	No visible vibration			
	22	560	Undefined	<1/64		
Haynes Alloy Number 25	10	190	13-17	1/16-3/32	Between 29.5-30.0	Between 725-750
	15	320	12	3/32		
	20	465	14	5/32		
	25	600	14	3/32		
	30	750	9	<1/64		
Nichrome V	10	220	26	1/32-1/16	23.5	660
	15	408	16-18	1/16-3/32		
	20	510	17	5/32		
	25	705	No visible vibration			
	30	805	No visible vibration			

[a] Vibration took place in only one plane on heating cycle from room temperature to 790°C; on cooling from 790°C to room temperature vibration occurred in all planes perpendicular to the wire between 460° and 135°C.

Xenon

Experimental Chromatograph Two experiments were made on an annular column with a cross-section area of 2.96 square centimeters and length of 19 centimeters. The adsorbent was 50/60 mesh coconut charcoal. With a feed of 1000 cubic centimeters, the ratios of krypton-85 concentration in the feed to that in the product were 153 and 162.

The experiments were repeated using a tubular column with a cross-sectional area of 5.067 square centimeters and a length of 19 centimeters. The adsorbent was 6/14 mesh Columbia AC-grade carbon. With one-liter feed samples separation factors of 779 and 804 were obtained in two experiments. When 500-cubic centimeter feed samples were employed, it was impossible to determine the xenon peaks. Hence, for the 500-cubic centimeter experiments, an arbitrary decision was made to switch the stream into the product trap. Two experiments gave separation factors of 904 and 1,186. There was still a 64 per cent recovery of product in the run which had a 1,186 separation factor.

Thermal Diffusion Theory

The performance of a thermal diffusion column is strongly dependent upon the convective velocity present in the column. In the theory of the operation of a column which was recently developed at Mound Laboratory, a second order differential equation for the velocity was derived. Although this equation must be solved by numerical methods, the functional dependence of the velocity on the geometry of the column can be determined by simple considerations. Consider the cylindrical solution as the column approaches a plane case, i.e., as $(r_1 - r) \rightarrow X$, where X is a cartesian coordinate. The radial coordinate r as a function of the temperature is given by the equation:

$$r = r_1 e^{-1/Q \int_{T_1}^{T} \lambda dT}$$

where

$$Q = \frac{1}{ln(r_1/r_2)} \int_{T_1}^{T_2} \lambda dT$$

Using the series expansion for the exponential,

$$(r - r_1) = r_1 \ln (r_1/r_2) \left[\frac{\int_{T_1}^{T} \lambda dT}{\int_{T_1}^{T_1} \lambda dT} \right] + ½ \left[\ln (r_1/r_2) \right]^2 \left[\frac{\int_{T_1}^{T} \lambda dT}{\int_{T_1}^{T_2} \lambda dT} \right]^2$$

For the plane case (see Figure 1),

$$X = \frac{w \int_{T_1}^{T} \lambda \partial T}{\int_{T_1}^{T_2} \lambda dT}$$

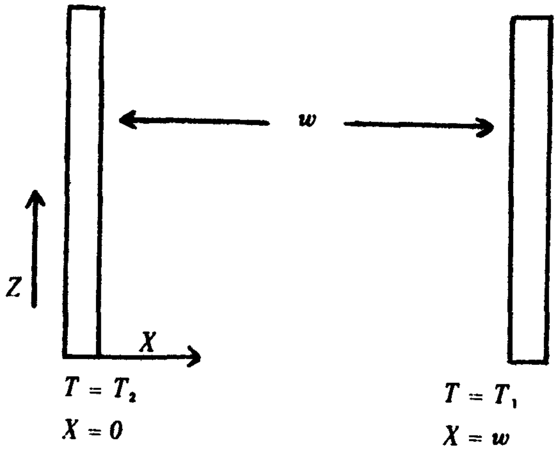

Figure 1. *Two Parallel Plates Separated by a Distance w*

Thus, in order for $(r_1 - r)$ to approach X, ln (r_1/r_2) must approach zero or (r_1/r_2) must approach one. Also, as (r_1/r_2) approaches one, the quantity r_1 ln (r_1/r_2) corresponds to w (the distance between the two parallel plates in the plane case). This analogy may be seen by noting that all terms in the expansion of the cylindrical case contain a power of ln (r_1/r_2) in the numerator. Since this approaches zero in the limit, all terms also approach zero. However, the assumption that the plane case is the limit is consistent when it is recognized that r_1 approaches infinity for the plane case, and thus the first term actually does not disappear. Instead a term is left which is identical in form to the plane case. The indeterminate (infinity times zero) quantity is then analogous to the arbitrary parameter w. The foregoing analysis has shown that the geometry of a column can be represented by the quantities (r_1/r_2) and r_1 ln (r_1/r_2). The quantity (r_1/r_2) is a measure of how much the column deviates from two parallel plates, and r_1 ln (r_1/r_2) corresponds to the distance between the two plates. Since the convective velocity between two parallel plates is proportional to w, one would expect that for fixed (r_1/r_2) the velocity in a column will be proportional to r_1 ln (r_1/r_2). Also, for r_1 ln (r_1/r_2) constant, the velocity in a column will approach the velocity between two parallel plates which are separated by a distance r_1 ln (r_1/r_2) as (r_1/r_2) approaches one.

ALPHA AND NEUTRON SOURCE DEVELOPMENT

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

A summary was given in December, 1962, of an analysis of possible errors in the determination of neutron emission strengths by comparison with a standard when using a long counter as the detector. In determining the error due to deviation from point-source geometry it was assumed that the error introduced by ignoring neutron scattering within a source would be negligible. Further analysis has shown this error may not be negligible; therefore, it needs to be evaluated.

The counting rate for a finite cylindrical source is proportional to

$$\int_{\substack{source\\volume}} \int_{\theta} \frac{\left[\exp\left\langle -\sum \mu t\,(\theta)\right\rangle + U\,(\theta)\right] \sin\theta}{\left[r'\,(\theta)\right]^{2}} \, d\theta d\,V$$

where $r'\,(\theta)$ is the distance between an elemental source volume and the effective center of the detector; $t\,(\theta)$ is the distance of neutron travel within one of the materials making up the source, and μ is the total macroscopic cross section for this material; θ is the angle of orientation of the source axis of symmetry to the detector axis of symmetry. The exponential is the attenuation factor of the original neutron beam within the source; the factor $U\,(\theta)$ represents neutrons emitted from the source in direction θ which either had been previously scattered within the source or produced by secondary reactions within the source.

The term $U\,(\theta)$ will be a function of source geometry, differential cross sections, and the angular distributions of neutrons from secondary reactions. This term should be a relatively slowly varying function of θ when compared with the attenuation factor, and for a first approximation it will be assumed constant. Generally the principal material within a source is the target material for the $(n,\ a)$ reaction. In this first approximation other materials within the source will be ignored. The problem is now simplified to the evaluation of the following integral:

$$\int_{\substack{source\\volume}} \int_{\theta} \frac{\exp\left[-\mu\, t\,(\theta)\right] \sin\theta}{\left[r'\,(\theta)\right]^{2}} \, d\theta d\,V$$

where t and r' are both functions of θ.

A computer program is being written to obtain an approximate solution by numerical integration and thereby determine more correctly the calibration error due to source geometry.

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.

Krypton-85

Krypton-85 Analysis by Gamma Counting The gamma counting method of analyzing krypton-85 in xenon [MLM-CF-61-6-281] has been modified. Gas samples in 20-milliliter glass containers are gamma counted using a 400-channel analyzer and a two-inch by two-inch sodium iodide well crystal calibrated to five kev per channel. The gamma counting rate per millimeter of sample in the kryton-85 photopeak (channels 80-129) is multiplied by a predetermined factor to yield the atom per cent of krypton-85.

The calibration factor was determined by comparing the gamma counting rate of five samples with results from internal gas proportional counting. The average was 7.32 (±0.27) x 10^{-7}.

Low-level Krypton Counting A low-level counting system was built for the detection of trace amounts of krypton-85 in xenon. The goal is to detect 10^{-15} atom per cent krypton-85, but due to radioactivity present in the construction materials and in the lead shielding, the level of detectability is only 10^{-13} atom per cent.

The effects of shielding and anticoincidence in the reduction of the background counting rate were determined for W. H. Johnston one-liter proportional chambers. The chambers were filled with P-10, a commercially available proportional counting gas (90 per cent argon, 10 per cent methane), at 600 millimeters of mercury and 0°C. One-hour background counting studies were first made in the open room, then inside the low-level lead shield, and finally inside the shield using an anticoincidence Geiger ring. A high background counting rate of 91 counts per minute in the final test was believed to originate from natural radioactivity in the lead shielding and radioactive contamination in the gas handling system.

In an attempt to reduce the high background counting rate, a glass frit (15-micron pore size) was inserted in the lines. Proportional counting (P-10) gas was subjected to the contamination in the gas handling system for approximately 18 hours; then it was expanded into the Johnston chamber through the glass frit. Two hours later a background count of 76 counts per minute was obtained in the low-level lead shield with the anticoincidence ring in operation. The frit caused an activity reduction of about 15 counts per minute. The system was purged with dry nitrogen gas for about eight hours and refilled with P-10 gas. The gas was expanded through the glass frit and counted; the rate was 48 counts per minute, an additional 28 counts per minute decrease in the background. Most of the 48 counts per minute is still thought to be natural contamination of the lead shield.