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SUMMARY

ISOTOPE SEPARATION AND PURIFICATION

Carbon-13 Using six hot-wire columns and three concentric tube thermal diffusion columns a cascade system was arranged to produce 0.04 gram of 90 per cent carbon-13 per day using methane as the feed gas.

The ten liter shipment of purchased methane enriched to 60 per cent carbon-13 was received. This gas will be enriched to 90 per cent carbon-13 at Mound Laboratory.

Before removing the equilibrated gas from the concentric tube columns in preparation for using methane enriched in carbon-13 as feed material, a sample of methane taken from the bottom of the last column contained greater than 65 per cent carbon-13.

RADIOELEMENTS

Hydrolysis and Residue Adsorption of Protactinium The hydrolysis of protactinium is completely controllable and reversible and can serve as the basis for its separation from other elements, particularly its decay products. The tendency to hydrolyze is not a unique characteristic of protactinium, but is exhibited, under appropriate conditions, by thorium-227 and radium-223 at trace levels.

Traces of protactinium in one normal sulfuric acid can be removed from solution by a coarse glass wool filter through which the decay products pass readily. The reverse is true if the sulfuric acid concentration is increased to six normal.

The desorption of protactinium from platinum is a function of the reagent, the reagent concentration, and the amount of protactinium adsorbed. The relative solubility of protactinium in various reagents increases in the order: $\text{HNO}_3 < \text{HCl} < \text{H}_2\text{SO}_4 < \text{H}_2\text{C}_2\text{O}_4 < \text{HF}$.

Growth Constants of Actinium-227 Equations for computing the growth of the principal alpha-emitters in the actinium-227 decay chain have been recalculated based on the recently redetermined half-lives of actinium-227, thorium-227 and radium-223.

Waste Disposal Research Several laboratory experiments on waste disposal problems have indicated that radioactivity levels in influent water can be significantly reduced by precipitating aluminum hydroxide as well as bismuth hydroxide in the hydrolysis cell. The aluminum hydroxide effectively removed zinc-65 from the influent water (ZN^{65} is a major radioactive impurity in irradiated aluminum cans from the polonium process).

Potassium Plutonium Sulfate The solubility product constant of potassium plutonium sulfate in lithium sulfate was determined to be $5.00 \pm 0.33 \times 10^{-18}$.

ANALYTICAL

Calorimetry Additional measurements were made on the "stretching effect" using a quasi-calorimeter built for this purpose. The stretching effect is a change in the thermal properties of materials of construction believed to be related to the coefficient of thermal expansion. Styrofoam for example, has a large "stretching effect", Lucite has almost none.

SEPARATION AND PURIFICATION

Mound Laboratory is responsible for the separation and sale of purified helium-3 throughout the free world. The isotopes of the other noble gases are available for distribution in research quantities. Methods of isotope separation and purification are being studied.

CARBON ISOTOPE SEPARATION

Thermal Diffusion The objectives of the carbon-13 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. Two cascaded hot wire columns are used for the removal of heavy gaseous impurities in methane, such as nitrogen, carbon monoxide and ethane. Feed which is 99 per cent methane enters the middle of the top half of the system at about 230 milliliters per hour. Waste is drawn off at the bottom at less than 10 milliliters per hour and high purity methane is drawn off at the top and frozen into 2.5 liter cylinders.

As a result of column studies the three-stage unit of six hot-wire columns was shut down and repiped to form a cascade of 2-2-1-1. This unit and the three concentric tube unit are expected to enrich natural methane to a concentration of about 90 per cent carbon-13.

A methane separation run of 67 days has been completed on the three 24-foot concentric tube thermal diffusion columns in cascade. Each column has a 0.75 inch diameter hot wall at 400°C and a 1.25 inch diameter cold wall at 15°C.

Purified natural methane (0.01 to 0.04 per cent impurities) was fed at the rate of three to four liters per day across the top of the first column. Samples were taken at least weekly at the top and bottom of the third column.

At the start of the run the mass-17 enrichment at the bottom of the last column was 11.7 per cent. The bottom composition rose to 29.2 per cent after 20 days. From this point accumulation of carbon dioxide at the bottom began to interfere with the isotope analysis, and the methane content dropped to less than 10 per cent. At 46 days of operation 200 cubic centimeters of impurities were removed from the bottom of the column, and 100 cubic centimeters were removed at 53 days.

After 67 days the column system was emptied in small increments and a composition profile was determined. Results are given in Table 1. The highest measured isotope enrichment was 54 per cent; the extrapolated results indicate that in the absence of impurity interference, the bottom enrichment would have been 65 to 70 per cent.

Table 1
CONCENTRATION PROFILE

Sample Number	Location (%) of Column Length From Top	Reported Methane Content (%)	Reported Mass-17 Content of Methane (%)
1	0 (top)	99.8	0.85
2	51.7	98.7	4.85
3	75.9	99.7	17.36
4	85.7	95.6	31.25
5	95.0	15.9	53.72
6	100 (bottom)	3.0	40.69

It is not clear whether or not the system was in a steady-state condition at the conclusion of the experiment. Sampling of the system was equivalent to a production rate of roughly 20 cubic centimeters per week, which is a significant rate relative to the isotope transport rate of the column. The removal of impurities, therefore, caused a large disturbance which had not disappeared at the conclusion of the experiment.

Methane Purification Three additional runs were made with the methane purification system and are indicated as 23, 24 and 25 in Table 2. Runs 21 and 22 were discussed previously and are included to report the analytical results on the products. Runs 23 and 24 utilized the new larger process trap but did not use bubbling helium, carbon boiling chips, or magnetic stirring as had been used on some previous runs. The results of these two runs indicate that rather large batches of methane can be purified to about 99.8 per cent without helium bubbling by drawing off one-third of the original material as raffinate from a process trap of suitable geometry.

Run 25 was an attempt at a simple purification method and gave poor results. In this run, chemically pure gas was passed through a molecular sieve and a carbon trap, both at dry ice temperature.

Table 2

METHANE PURIFICATION

Experiment Number	Feed Composition		Product Composition		Remarks
	Methane (%)	Carbon-13 (%)	Methane (%)	Carbon-13 (%)	
21	99.2	1.05	99.8	1.05	One-third liquid methane boil off.
22	99.6	1.04	99.6	1.04	Through traps only.
23	99.2	1.05	99.9	1.07	One-third liquid methane boil off.
24	99.2	1.05	99.8	1.07	One-third liquid methane boil off.
25	99.2	1.05	99.2	1.04	Through traps only.

THEORETICAL

A new theory of operation of the thermal diffusion column was developed over the past year. The computer program to numerically calculate the concentration distribution in the thermal column has been started. The program is being written in sections to facilitate debugging procedures. The section which contains sub-routines for viscosity η , thermal conductivity λ , ordinary diffusion D , and thermal diffusion factor α , has been written and debugged. These sub-routines are based on the Chapman-Enskog¹ equations for a binary mixture. The separate sections of the complete program will be used to study the assumptions on the Jones and Furry² theory of the thermal column. One assumption made by Jones and Furry is that the transport properties cited above are independent of the concentration of the components in the mixture. The Chapman-Enskog theory postulates that only the ordinary diffusion coefficient D is independent. The concentration

¹Hirschfelder, Curtiss and Bird, "Molecular Theory of Gases and Liquids", John Wiley & Sons, New York 1954: (See Section 8.2).

²Furry, W. H., and R. Clark Jones, *Phys. Rev.*, 69, p. 459 (1946).

dependence of helium-3-helium-4 and neon-20-neon-22 mixtures for the viscosity, thermal conductivity, and thermal diffusion factor are shown in Figure 1.

The validity of the Jones and Furry assumption cannot be ascertained from Figure 1 alone, however, it would appear to be justifiable for isotopic systems with mass number greater than 20. Two interesting properties are shown by the graph:

1. All three properties are essentially linear functions of the concentration.
2. Since the quantities η and λ appear as a ratio in the column theory, the fact that they change in the opposite sense serves to compound errors in the old theory.

Figure 1

RELATIVE CHANGE OF TRANSPORT PROPERTY WITH CONCENTRATION

RADIOELEMENTS

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

HYDROLYSIS AND RESIDUE ADSORPTION OF PROTACTINIUM

One of the most frequently cited characteristics of protactinium is its tendency to hydrolyze in aqueous solution and to deposit on the sides of glassware and other containing vessels. This behavior is shown in the following example:

A concentrated sulfuric acid solution containing approximately 1.5 milligrams of protactinium per milliliter was diluted with distilled water to yield a solution approximately one normal in sulfuric acid and containing approximately seven micrograms of protactinium per milliliter. The solution was mixed thoroughly.

The solution was sampled immediately after dilution, and the gamma spectrum was recorded (Fig. 2, Spectrum A). The solution was allowed to stand undisturbed for two days, when it was again sampled, care being taken to draw the liquid from the upper portion without disturbing the main body of the solution. The gamma spectrum of the second fraction is shown in Figure 2, Spectrum B.

The solution was thoroughly mixed and sampled again. The gamma spectrum of the third sample was identical with that of the first (Figure 2, Spectrum A).

Comparison of the two spectra in Figure 2 shows the striking diminution of the 27-kev photopeak as compared with the peak at 90 kev. The peak at 300 kev in Spectrum A has been shifted to 280 kev in Spectrum B. These changes indicate that the protactinium has hydrolyzed to the extent indicated by the relative heights of the peaks at 27 kev, while the decay products which accumulated during the 18 months since the protactinium was purified, were relatively unaffected.

Figure 2

HYDROLYSIS IN 1 N H_2SO_4

A coarse filter was prepared by introducing a small plug of Pyrex glass wool into a medicine dropper and packing the glass wool sufficiently to provide a gravity flow rate of approximately one milliliter per minute. The one normal sulfuric acid solution of protactinium was mixed thoroughly, and a sample was passed through the filter.

The filtrate was collected in a glass vial, and its gamma spectrum was recorded (Figure 3, Spectrum A). The filter was washed with two half-milliliter portions of 0.01 N hydrofluoric acid and the fluoride solution was collected in another glass vial. Its gamma spectrum is shown in Figure 3, Spectrum B.

The two spectra of Figure 3 show clearly the separation of protactinium from its decay products. Spectrum B shows the characteristic photopeaks of protactinium-231 at 27, 95, and 300 kev, while Spectrum A shows, in addition to the small peak at 27 kev (due to protactinium), the peaks characteristic of actinium-227 and its decay products (50, 85, 156, 285, and 350 kev).

A sample of the one normal sulfuric acid solution of protactinium was transferred to a glass vial and evaporated, at 100°C., to its minimum volume. The vial was cooled, and six normal sulfuric acid was added to bring the solution back to its original volume. The solution was mixed thoroughly, stoppered, and allowed to stand undisturbed for four days.

The solution was filtered through a coarse filter of Pyrex glass wool, and the filtrate was collected in a glass vial. The gamma spectrum is shown in Figure 4, Spectrum A. The filter was washed with one normal nitric acid and the wash was collected in a second glass vial (Figure 4, Spectrum B).

Figure 4 again shows the separation of protactinium from its decay products; in this case, however, the fractions are reversed as compared with those of Figure 3. Spectrum A represents the activity which passed through the glass wool filter in six normal sulfuric acid, while spectrum B represents the activity retained by the filter, and recovered in one normal nitric acid.

Figure 3

HYDROLYSIS IN 1 N H_2SO_4

It is to be noted that spectrum A of Figure 4, exhibits, in addition to the usual protactinium photopeaks, the small peaks at 50 and 156 kev, characteristic of thorium-227 and radium-223, respectively. The radium-223 peak (156 kev), however, is attributable largely to growth from thorium-227, since the two spectra of Figure 4 were recorded approximately one month after the separation. In the gamma spectrum of the filtrate immediately after separation, the 156 kev photopeak was virtually absent.

The results represented by the spectra of Figures 2, 3, and 4 show that, far from being an uncontrollable nuisance, the hydrolysis of protactinium has a useful application, not only in the separation from its decay products but in the separation from other impurities as well.

Furthermore, as shown in Figure 4, precipitation at trace levels is not unique to protactinium, but is exhibited, under appropriate conditions, by the alkaline earth elements; in this case, radium-223. It is also apparent that the hydrolysis of protactinium is not irreversible, since the hydrolyzed protactinium of Figure 2 was completely solubilized by a relatively mild change in the sulfuric acid concentration.

To provide a convenient source of purified protactinium in a solution free of sulfuric acid, the one normal sulfuric acid solution was passed through a glass wool filter, and the filtrate was discarded. The filter was washed with distilled water and 0.1 normal nitric acid, and the residual nitric acid was washed away with distilled water. The protactinium was recovered from the filter in 0.01 normal hydrofluoric acid, and stored in a styrene vial.

The method of residue adsorption³ was applied to a determination of the relative solubility of protactinium in various reagents and reagent concentrations.

Figure 4

HYDROLYSIS IN 6 N H_2SO_4

³Kirby, H. W. "Residue Adsorption I. Separation of Strontium-90 and Yttrium-90". *J. Inorg. Nucl. Chem.* 25, 483 (1963).

Several platinum disks were cleaned by agitation for five minutes in alcoholic potassium hydroxide. They were rinsed thoroughly with distilled water and dried with absorbent paper. Each disk was masked with a glass vial 15 mm. in diameter and sprayed with Krylon Crystal-Clear Spray Coating (a mixture of methyl and n-butyl methacrylates). The mask was removed and the coating was dried for a few minutes at 90°C. The uncoated area was covered with 0.25 ml. of 1 N HNO₃, heated for one minute at 90°C., and rinsed thoroughly with distilled water. The disk was dried on a hot plate at 90°C.

A sample consisting of 9.3 micrograms of protactinium-231 in 0.01 N HF was deposited in the open area of each platinum disk and evaporated to dryness at 90°C. One-half milliliter of distilled water was added to each residue, and the solution was again evaporated to dryness at 90°C. Heating was continued for five minutes after the last visible trace of moisture had evaporated from the surface.

The residue was covered with 0.5 ml of the reagent indicated in Table 3 and heated for two minutes at 90°C. The solution was transferred to a styrene vial with the aid of a transfer pipette. The reagent addition, heating, and transfer were repeated.

Each residue was leached successively with two 0.5-ml. portions of several concentrations of the same reagent. The gross gamma-counting rate between 0 and 400 kev was determined for each reagent concentration and the results are reported in Table 3 as a percentage of the amount of protactinium remaining after leaching by the last previous concentration of the same reagent. The counting rate of the protactinium remaining on the platinum disks was determined by alpha-counting and compared with the alpha-counting rate of a standard sample of the original protactinium solution.

Table 3

PERCENTAGE DESORPTION OF PROTACTINIUM-231 FROM PLATINUM BY VARIOUS REAGENTS

Reagent Normality	HNO ₃	Na ₂ EDTA	HCl	H ₂ SO ₄	H ₂ C ₂ O ₄	HF
0.00	3.4	9.8	-	4.9	-	5.7
0.01	0.9	6.7	5.7	1.5	9.8	96.2
0.1	0.3	4.1	0.9	2.6	33.0	92.6
1	1.6	-	3.2	63.1	66.0	-
3	4.2	-	9.3	73.2	-	-
6	10.8	-	76.3	33.8	-	-
Residual ^a	80.2	76.7	19.4	6.0	18.0	0.3

^aPer cent of total originally deposited.

The results in Table 3 indicate the relative solubility of protactinium in the various reagents. Because of the limited solubility of stoichiometric disodium ethylenediaminetetraacetate (Na₂EDTA) it was not possible to check the solubility of protactinium in this reagent at concentrations comparable to those of the other reagents. However, omitting Na₂EDTA, and comparing the results at 0.1 normal for the other reagents, the relative solubility of protactinium appears to increase in the order:

The three to 10 per cent desorption by the first reagent concentration in each case probably results from the fact that the protactinium was initially deposited from a solution which was 0.01 normal in hydrofluoric acid; hence, the initial desorption removed not only protactinium but also the residual hydrofluoric acid and fluoride ion.

A similar series of experiments was carried out with an actinium equilibrium mixture (AEM) consisting of a one normal nitric acid solution of actinium-227 in secular equilibrium with its decay products (radium-223 and thorium-227). The results are shown in Table 4.

Table 4

PERCENTAGE DESORPTION^a OF ACTINIUM EQUILIBRIUM MIXTURE FROM PLATINUM BY VARIOUS REAGENTS

Reagent Normality	HNO ₃	Na ₂ EDTA	H ₂ C ₂ O ₄	HF
0.00	61.1	41.6	40.9	52.4
0.01	28.1	42.0	52.0	24.6
0.1	4.2	10.2	4.7	3.7
1	2.9	-	0.9	0.9
3	1.1	-	-	-
6	0.7	-	-	-
Residual	0.6	6.1	1.5	18.5

^aPer cent of total originally deposited

It should be noted that, in the case of AEM, the gross percentages are relatively meaningless unless they are coupled with percentages for the individual radioisotopes composing the mixture. For example, Figure 5 shows the spectrum of the platinum disk leached with 1 N HF, showing the characteristic thorium-227 peaks, including an L X-ray at approximately 15 kev.

Figure 5

RESIDUE ADSORPTION: TH²²⁷ RESIDUE FROM AEM AFTER DESORPTION WITH 1 N HF

It is apparent, however, from a comparison of Tables 3 and 4, that a separation of protactinium from its decay products can be readily made by residue adsorption and appropriate selection of the reagent and reagent concentration used in leaching.

The significance of reagent concentration is illustrated by the following experiment:

A sample of AEM in 1 N HNO₃ was deposited on each of two platinum disks which had been cleaned and coated as described above. The solution was dried at 90°C., and the residue was covered with 0.5 ml. of distilled water. The solution was again dried at 90°C. and heating was continued for five minutes after the last visible trace of moisture had evaporated.

To one of the residues a sample of protactinium-231 in 0.01 N HF was added, and the solution was evaporated to dryness at 90°C. The residue was covered with 0.5 milliliter of distilled water and dried. The residue was heated for five minutes at 90°C., and 0.5 ml. of 1 N HNO₃ was added. The solution was evaporated to dryness and heated for an additional five minutes at 90°C.

The residue on each platinum disk was leached twice with 0.5-ml. portions of distilled water, which were heated two minutes at 90°C. and transferred to a styrene vial (Figure 6).

Each residue was leached with two 0.5-ml. portions of 0.01 N HNO₃ (Figure 7), 0.1 N HNO₃ (Figure 8), and 1 N HNO₃ (Figure 9). Finally, the residue on the disk which had originally held AEM only was leached with 3 N and 6 N HNO₃ (Figure 10, Spectrum A) and the residue on the disk to which both AEM and Pa²³¹ had been added was leached with 0.01 N and 0.1 N HF (Figure 10, Spectrum B).

The two spectra in Figure 6 are nearly identical, except for a small difference in the magnitudes of the gamma photopeaks. There is no indication in Spectrum B that any significant amount of protactinium was desorbed in distilled water. The same is true in Figure 7, although the difference in the peak heights is more pronounced. Protactinium first appears in Figure 8 (Spectrum B), where a deflection in the region of 27 kev indicates that a small amount of protactinium was desorbed by 0.1 normal nitric acid. The 27 kev peak is quite pronounced in Spectrum B of Figure 9, but the spectrum still represents a mixture of protactinium and its decay products, with the latter predominant, as indicated by the relative heights of the peaks at 95 and 290 kev. In addition, the presence of peaks at 50 and 156 kev indicates that thorium-227 is still in the process of being desorbed. This is confirmed by the spectrum of the residual protactinium (Figure 10), which again shows the presence of thorium-227 by peaks at 50 and 156 kev.

Figure 6

DESORPTION IN H₂O

Figure 7

DESORPTION IN 0.01 N HNO_3

Figure 8

DESORPTION IN 0.1 N HNO_3

Figure 9

DESORPTION IN 1.0 N HNO₃

Figure 10

RESIDUAL AFTER DESORPTION IN 1.0 N HNO₃

Nevertheless, it is evident that a considerable degree of purification of protactinium, with relatively little loss, can be achieved by selective desorption of the decay products in dilute nitric acid.

It should be noted that residue desorption differs from dissolution in that the amount of solute desorbed is a function not only of the volume and concentration of the solvent but also of the amount of solute initially adsorbed. This is illustrated in the following experiment:

A sample of AEM in one normal nitric acid was evaporated to dryness at 90°C on a platinum disk. The residue was covered with a sample of protactinium in a mixture of 0.002 normal hydrofluoric acid and 0.001 normal sulfuric acid. The solution was evaporated to dryness. The residue was covered with 0.25 ml of three normal ammonium hydroxide and evaporated to dryness. Heating was continued for five minutes after the last visible trace of moisture had evaporated.

The residue was leached twice with 0.5-ml portions of one normal nitric acid heated for five minutes at 90°C. and transferred to a second platinum disk. The second platinum disk was dried, covered with 0.25 milliliter of three normal ammonium hydroxide, dried, and leached with one normal nitric acid as before. The leachings were transferred to a third platinum disk.

Gamma spectra of the residues on the three platinum disks were run with a NaI(Tl) detector having a 0.001-inch aluminum window (Figures 11, 12, and 13).

In Figure 11, the gamma spectra of the first two platinum disks are compared. Both show the characteristic spectrum of protactinium-231, essentially free of decay products. (The platinum K-ray at 65 kev is not to be confused with a gamma photopeak.) Figure 12 compares the gamma spectra of the second and third platinum disks. It is seen that the third disk, containing nearly all of the AEM, still shows a small peak at 27 kev, indicating the presence of protactinium.

It is apparent that, although approximately 85 per cent of the protactinium remained on the first platinum disk, as shown in Figure 11, approximately the same percentage of the protactinium which had been transferred to the second disk remained adsorbed when the AEM was transferred to the third disk.

Figure 11

RESIDUE ADSORPTION: SEPARATION OF P_a AND AEM DESORPTION IN 1 N HNO_3

RESIDUE ADSORPTION: SEPARATION OF P_0 AND AEM-DESORPTION IN 1 N HNO_3 ,

RESIDUE ADSORPTION: SEPARATION OF P_0 AND AEM-DESORPTION IN 1 N HNO_3 ,

In Figure 13, the gamma spectra of the two major fractions are compared, with Spectrum III displaced vertically to avoid overlapping. Figures 11, 12, and 13 together confirm the statement above to the effect that residue desorption and dissolution are not identical. Whereas the AEM moved nearly quantitatively from the first platinum disk to the second and from the second to the third, the protactinium which was solubilized and transferred to the second disk was not transferred, when treated in an identical manner, to the third disk. These results are in accord with those found for yttrium hydroxide, where it was shown that residue adsorption follows the classical isotherm of Freundlich.

As noted above, in connection with the data in Table 5, gross counting rates have relatively little significance in describing the adsorption and desorption of AEM, since the three major components (Ra^{+2} , Ac^{+3} , Th^{+4}) exhibit different chemical behavior even at the submicrogram level. Gamma spectrometry can provide only semi-quantitative information about the behavior of radium-223 and thorium-227 and none at all regarding actinium-227. Alpha spectrometry is of only slightly more value because of the low branching ratio (1.2%), the low energy (4.94 mev) of the actinium-227 alpha, and the rapid growth of radium-223 and its decay products.

Work is in progress to determine the residue adsorption behavior of AEM by the method of differential decay. The growth constants necessary for this determination have been recomputed on the basis of half-lives of actinium-227, thorium-227, and radium-223 recently redetermined at Mound Laboratory.

GROWTH CONSTANTS OF ACTINIUM-227

The growth constants for the principal alpha-emitters in the actinium-227 decay chain have been recalculated to take into account the new half-life values of actinium-227, thorium-227 and radium-223 as determined at Mound Laboratory.

The alpha growth of actinium-227 is given by the following equation:

$$\frac{a_t}{N_o \lambda_1} = 5.01743898 e^{-\lambda_1 t} - 11.16418166 e^{-\lambda_2 t} \\ - 0.00002223 e^{-\lambda_2 t} + 6.15865636 e^{-\lambda_3 t} \\ + 0.00006408 e^{-\lambda_4 t} + 0.00000001 e^{-\lambda_7 t}$$

The alpha growth of thorium-227 is given by the following equation:

$$\frac{a_t}{N_o \lambda_2} = 11.27316533 e^{-\lambda_2 t} - 10.27550923 e^{-\lambda_3 t} \\ + 0.00000794 e^{-\lambda_4 t} + 0.00234455 e^{-\lambda_6 t} \\ - 0.00000861 e^{-\lambda_7 t}$$

The growth of thorium-227 from initially pure actinium-227 is given by the following equation:

$$\frac{N_2 \lambda_2}{N_o \lambda_1} = 0.99033247 \left(e^{-\lambda_1 t} - e^{-\lambda_2 t} \right)$$

The growth of radium-223 from initially pure actinium-227 is given by the following equation:

$$\frac{N_3 \lambda_3}{N_0 \lambda_1} = 1.00377579 e^{-\lambda_1 t} - 2.54255474 e^{-\lambda_2 t} \\ + 0.00001532 e^{-\lambda_{2a} t} + 1.53876363 e^{-\lambda_3 t}$$

The growth of radium-223 from initially pure thorium-227 is given by the following equation:

$$\frac{N_3 \lambda_3}{N_0 \lambda_2} = 2.56737491 \left(e^{-\lambda_2 t} - e^{-\lambda_3 t} \right)$$

The half-lives used in computing the growth coefficients are:

$$\begin{aligned} (Ac^{227}) T_1 &= 21.772 \text{ years} \\ (Th^{227}) T_2 &= 18.729 \text{ days} \\ (Fr^{223}) T_{2a} &= 21 \text{ minutes} \\ (Ra^{223}) T_3 &= 11.434 \text{ days} \\ (Rn^{219}) T_4 &= 3.92 \text{ seconds} \\ (Po^{213}) T_5 &= 0.00183 \text{ second} \\ (Pb^{211}) T_6 &= 36.1 \text{ minutes} \\ (Bi^{211}) T_7 &= 2.16 \text{ minutes} \end{aligned}$$

POLONIUM-208 AND POLONIUM-209 IN IRRADIATED BISMUTH

The energy and abundance of the low energy alpha particle group in the decay of polonium-209 were measured in several sources of mixed polonium isotopes. The measurements were made with a semiconductor detector-low noise amplifier system, fed to a multichannel analyzer. The results are given in Table 5. The errors in the abundance values are high due to the statistics of counting. The accuracy of the abundance cannot be significantly improved with a counting method at the present time with these sources. Low energy tailing of the main polonium-209 alpha group, and the alpha group of polonium-210 increases the background counting rate at 4.617 Mev.

Table 5

ENERGY AND ABUNDANCE OF THE LOW ENERGY ALPHA GROUP IN Po²⁰⁹

<u>Sample</u>	<u>Abundance, %</u>	<u>Energy, Mev.</u>
1916	0.69 ± 0.05	4.615 ± 0.006
2291	0.56 ± 0.04	4.618 ± 0.006
2301	0.57 ± 0.04	4.618 ± 0.006
Average	0.61	4.617

Coincidentally with the measurements on the low energy alpha group given above, the alpha activities of polonium-208, polonium-209, and polonium-210 in the three samples were redetermined, with much greater accuracy for polonium-208 than previously reported (MLM-1145). The relative yields of the three isotopes in bismuth irradiated in a natural uranium fueled reactor are being recalculated from these measurements, and will be reported soon.

Approximately 70 millicuries of polonium-208 were returned to Mound Laboratory from Los Alamos Scientific Laboratory. This material is part of the original cyclotron-produced polonium-208. The alpha-activity ratio, polonium-208/polonium-209 at the present time (defined as R_{A_t}) was measured by plating a small quantity of the polonium on a silver slide, and counting with a semiconductor detector. R_{A_t} was found to be 21.1 ± 0.1 . This is surprisingly high, and may have important implications in the determination of the half life of polonium-208 calorimetrically. The gamma-ray spectrum of the polonium-208 sample being used to determine the half life was compared to the spectrum of the Los Alamos polonium-208. The results indicate that R_{A_t} for the calorimetry source is at least 30. Computer analysis of the calorimetry data indicate that the ratio is about 16. Further work is in progress to reconcile these differences.

WASTE DISPOSAL RESEARCH

Highly radioactive nuclides in wastes from the polonium production area (including the irradiated aluminum jackets) were removed by treating the wastes in the HH cell. Formerly, bismuth hydroxide was precipitated from solution by adjusting the pH of the waste solutions to 12.0. This removed bismuth effectively, but since $\text{Bi}(\text{OH})_3$ is not a good carrier for the radioelements usually found in polonium waste solutions, most of the activity remained in solution, and created severe decontamination problems in the waste disposal area.

The effectiveness of various reagents and mixtures of reagents for removal of radioactivity is being monitored by alpha, beta, and gamma counting. The pH for maximum decontamination is being determined in the same manner.

Tests with solutions of irradiated aluminum show that decontamination factors approaching 1000 can be obtained by simply precipitating $\text{Al}(\text{OH})_3$ in the pH range 7.0 to 8.0. In this range, different radioactive species are selectively removed, as shown by gamma-ray spectrometry, but the alpha and beta counts remain approximately the same.

There is some evidence that low-energy beta particles are not being counted in the proportional counters used for estimating the beta activity, because of sample self-absorption. This is demonstrated by the differences in the decontamination factors calculated from beta and gamma counting results. The beta decontamination factors are generally higher. Self absorption also creates problems in the estimation of the true beta activity in the presence of alpha activity: some of the energy-degraded alpha particles are counted as beta particles. Further work is in progress on all phases of the waste disposal problems.

POTASSIUM PLUTONIUM SULFATE

The solubility study of $\text{K}_4\text{Pu}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ in two molar acid solutions of lithium sulfate (see MLM-1148) was reproduced. The solubility product constant of the compound was determined to be $5.00 \pm 0.33 \times 10^{-18}$ (or $\text{pK}_{\text{sp}} 17.3$) using the reported formation constants for the plutonium sulfate complexes. The " K_4 " value could not be accurately determined by the graphical method due to uncertainties in the experimental data. It was, however, shown to be very small. The experimental data and theoretical equations were submitted for computer analysis to evaluate all the formation constants for plutonium sulfate complexes.

The thermogravimetric analysis of $\text{K}_4\text{Pu}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ showed that a quantity of water greater than the theoretical amount was lost between 50° and 200°C . The material used for the original thermogravimetric study was two months old. The possibility that the excess weight loss above the theoretical amount was due to decomposition or peroxide formation caused by alpha radiolysis was investigated. Four months old $\text{K}_4\text{Pu}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ and freshly prepared $\text{K}_4\text{Pu}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ were analyzed by the thermogravimetric procedure. There appears to be no significant deviation between the two sets of points. Therefore, the high weight loss is probably not due to alpha radiolysis of the compound.

The differential thermal analysis (DTA) of $K_4Pu(SO_4)_4 \cdot 2H_2O$ (reported in MLM-1148) is being repeated at different rates to insure that equilibrium has been reached at each transition point on the curve. Samples of $K_4Pu(SO_4)_4 \cdot 2H_2O$, $Pu(SO_4)_2 \cdot 4H_2O$, K_2SO_4 and a mixture containing two parts of K_2SO_4 and one part of $Pu(SO_4)_2 \cdot 4H_2O$ have been submitted for DTA studies. Results of this experiment are not complete.

X-ray samples were taken from portions of K_2SO_4 , $Pu(SO_4)_2 \cdot 4H_2O$ and $K_4Pu(SO_4)_4 \cdot 2H_2O$. These compounds were ignited to temperatures where weight loss or crystal transformation occurred according to the DTA and TGA plots. The materials were then sampled for x-ray diffraction studies.

Half-Life of Pu-238 A preliminary study was made to determine the half-life of plutonium-238 by the specific activity method using potassium plutonium sulfate dihydrate.

In previous progress reports it has been shown that the stoichiometry of $K_4Pu(SO_4)_4 \cdot 2H_2O$ is definite and stable for at least three months. In addition, the preparation and recrystallization of the compound appears to purify the plutonium from uranium, neptunium and the fission products. These considerations would seem to make this double sulfate an excellent primary standard for determining the half-life by the specific activity method. Gross alpha counting and calorimetry were used to measure the specific activity of plutonium-238 in the compound. The results of this study, shown in Table 6, indicate that the half-life is in the range of 86.5 years.

Table 6
ESTIMATION OF Pu-238 HALF-LIFE
Alpha Counting

$K_4Pu(SO_4)_4 \cdot 2H_2O$ (grams)	Activity (d/m/ml)	Specific Activity (d/m/mg)	Half-Life (years)
0.5139	9.374×10^{10}	3.823×10^{10}	87.3
0.1473	5.475×10^{10}	3.910×10^{10}	85.3
0.1289	1.154×10^{11}	3.826×10^{10}	87.2
0.1512	1.378×10^{11}	3.843×10^{10}	86.8
0.1673	3.080×10^{10}	3.883×10^{10}	85.9
			Average 86.50

Calorimetry

$K_4Pu(SO_4)_4 \cdot 2H_2O$ (grams)	Power (watts)	Specific Power (watts/gram)	
2.8875	0.3950	0.5768	86.29
2.7721	0.3780	0.5749	86.57
2.8875	0.3949	0.5767	86.30
			Average 86.40

From the results of this preliminary study it seems that the half-life of plutonium-238 can be determined accurately and rapidly by this method. The accuracy of the method will depend on the purity of the compound, the accuracy of the mass spectrometric measurements and the accuracy of the calorimetric measurements.

ANALYTICAL

Methods of analyzing elements and compounds in support of other research and development programs are being developed.

CALORIMETRY

Stretching Effect Experiments with a quasi-calorimeter have added significantly to the understanding of the stretching effect. The stretching effect is manifested in the bridge potential as a tailing off of the cooling curve plotted on semilog paper. The stretching effect varies along the thermel from positive in the central portions to negative in the ends.

Four experiments were performed as follows: An assembly of ten chromel-p-constantan junctions, spaced 0.3 inch apart and held to a Styrofoam baffle by tape, was inserted in the quasi-calorimeter with Lucite ends. The cooling curve of each junction was obtained by a photocell amplifier driving a 10-millivolt recorder. The temperature profile was similar to that of Calorimeter 39 (MLM-1146).

A single thermocouple was attached to the Lucite end at the most negative temperature region of Experiment 1, the Styrofoam baffle was removed, and a cooling curve obtained. The stretching effect was 20 times smaller than for Experiment 1.

A layer of tape was wrapped around the Lucite ends. The thermocouple went negative by about half that of Experiment 1.

The tape was removed and a bare Styrofoam baffle inserted in the Lucite end. Again the thermocouple went negative by half that of Experiment 1.

The conclusions from the experiments are: Styrofoam baffles and (Scotch) tape have a stretching effect too great to use in calorimeters, Lucite has very little stretching effect, and contributions to the stretching effect can occur equally well on both inner and outer surfaces of the ends of the calorimeter. All baffles, especially Santocell-filled supermica forms, increase the stretching effect, but this could be due to changing the temperature gradient which is the driving force for the stretching effect. Calorimeter 39 has Styrofoam baffles wrapped with a layer of (Scotch) tape, but this is not the major source of the stretching effect. The major source is the Nylon insulation on the bridge wires. Calorimeter 90 was wound with enameled covered wire and has practically no stretching effect.

Calorimeter Calorimeter 90, completed in October 1962 (MLM-1144), is perhaps our best calorimeter. In physical dimensions it is very similar to Calorimeter 39, and has a sample space of 1.085 inch outer diameter by three inches long. The ends are made of Kel-F 81 with the bridge windings extending a length of 3-1/8 inches over each end. The aluminum central portion of the thermel is 4-5/8 inches long by 1.303 inch outer diameter by 1.245 inch inner diameter. The heater is of anodized aluminum 3-1/8 inches long by 1.245 inch outer diameter by 1.120 inch inner diameter, with grooves cut seven threads per inch with two departures. The heater wire, bifilar wound in the two grooves, is double Nylon covered #34 Manganin sealed with baking varnish. The bridge was wound with enameled #37 99-alloy wire in one layer of four wires, each wound at 48 threads per inch. The heater lead-wire forms are Kel-F 81, two inches long by 1.137 inch outer diameter with 0.04 inch wall thickness, grooved for the lead wires at three grooves per inch and 0.015 inch deep. The heater leads were Formvar covered #32 copper. The jackets were made from brass tubing 18 inches long by 1.75 inch outer diameter by 1.5 inch inner diameter, bored to 1.513 inches inner diameter with the jackets mounted to the lathe carriage and the boring bar turning in the chuck. The calorimeter leads were brought out through Kovar seals in the base. The jackets were mounted to an automatic sample loading device with a hermetically sealed Lucite cover.

Pertinent thermal and electrical properties are as follows: total bridge resistance-900 ohms; effective bridge resistance-380 ohms; heater resistance-105.4 ohms; thermal resistance-6.6°C per watt; sensitivity at five milliamperes bridge current-34,240 microvolts per watt; time to reach 0.01 per cent of equilibrium-1.5 hours; stretching effect-practically none.

Results obtained with two plutonium-238 half-life samples are excellent. The average of ten measurements on Sample 1 decayed to February 27, 1963, using an 86-year half-life is 1.13414 watts with a probable error per observation of 0.0025 per cent. Similarly, for Sample 2 results of 0.650130 watts with a probable error per observation of 0.002 per cent. The two samples were then measured simultaneously. The average of ten runs, again decayed to February 27, was 1.78431 watts with a probable error per observation of 0.0012 per cent. The sum of the individual results is 1.78427 watts, which is lower by only 0.002 per cent.

The calorimeter is therefore extremely linear and indicates the capability to measure in one half-life the half-life of a sample to 0.003 per cent. The automatic loading device was set for two cycles per day of six hours each for the sample and heater runs. The bridge potential remained constant from the fifth to the sixth hour to better than one part in 100,000.

It is expected that this calorimeter will be used indefinitely to measure half-lives of various samples. Some improvement, especially in the year-to-year confidence, will occur when the new guildline potentiometer (Type 9144, S.N. 22040) is installed this month. This potentiometer has been checked recently at the National Bureau of Standards and is accurate to 0.001 per cent or better.