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SUMMARY

Plastics and Adhesives Research

Adhesives Tensile strength and percentage elongation data for ten anhydride-cured epoxy and three polyol-cured polyurethane adhesive formulations, which had been aged for 12 months at ambient temperature, were obtained at -65°F, room temperature, and 160°F. These data showed that little or no degradation of the adhesive formulations took place during the 12-month period.

Flexible conductive adhesives were formulated with carbon black and silver fillers. These polyurethane formulations were heated to 160°F to determine whether the electrical resistance changed as a result of heating. The addition of carbon black to the formulation decreased the electrical resistance and increased the bond strength of the silver-filled formulation.

Plastics Five new fillers, i.e., two graphite fillers, one carbon filler, and two powdered silica fillers, were incorporated into diallyl phthalate formulations for experimental molding powders. Molded test specimens of these formulations were evaluated for tensile strength, percentage elongation, heat distortion temperature, impact strength, and arc resistance. The graphite and carbon-filled formulations had no appreciable increase in impact strength over the standard asbestos-filled material; however, they had higher tensile strengths and heat distortion temperatures. Silica-filled moldings had physical characteristics similar to the asbestos-filled plastic, but the formulation was unsatisfactory due to inclusions.

Radioelements Research

Polonium-208 and Polonium-209 The relative yields of polonium-208 and polonium-209 in reactor produced polonium-210 were redetermined by counting methods with greater accuracy than previously reported. A sample of polonium-208 was returned from Argonne National Laboratory. The sample contains about 15 microcuries of polonium-209 and will be used for accurately determining the half-life of that isotope. Two ion exchange procedures were developed for that purification of this polonium sample.

Single gamma-ray spectra were obtained of two different sources containing mixtures of polonium-208 and polonium-209. Prominent gamma energies were found at 75 kev, 130 to 140 kev, 260 kev, 580 kev, and 900 kev. The 75 kev peak is characteristic of x-ray spectra of polonium. Coincidence data are being obtained to assign the various radiations and nuclear energy levels to each of these isotopes.

Disposal of Polonium Process Waste The decontamination factors obtained with various treatments of wastes from the polonium process were investigated. Samples of a typical waste solution were treated by precipitation of various metal hydroxides at different pH levels. The alpha, beta, and gamma activities were measured and compared with the activity of the original solution. A single treatment of the waste will not lower the activity of the waste to an acceptable level. A decontamination factor of 4,000 will be required to reduce the activity sufficiently.

Actinium-227 The feasibility of using actinium-227 as a radioactive heat source was estimated from product data and from the power level of the isotope. The chief drawback to the use of actinium-227 is the limited supply of radium-226 that can be irradiated.

The half-life of actinium-227 was recalculated, giving a value of 21.7714 (+ 0.0056, - 0.0033) years. The half-life is based on data gathered over the last ten years and is considered to be accurate.

The growth and decay factors for the alpha-emitters in the actinium-227 decay chain have been recomputed on the basis of the new half-life values of actinium-227, thorium-227, and radium-223 recently determined at Mound Laboratory. New decay tables were developed for the decay of actinium-227, thorium-227, and radium-223 and for the growth of alpha activity from initially pure actinium-227 and pure thorium-227.

Differential decay data were obtained for the residue adsorption fractionation of actinium-227, thorium-227, and radium-223 in nitric and hydrofluoric acids. Preliminary work on a sequential residue adsorption separation of protactinium-231 and its principal decay products was completed. The residue adsorption technique is useful for the preparation of alpha sources having improved characteristics as standards.

Uranium-232 The power growth curve for uranium-232 was calculated.

Uranium-234 Two methods for separating and purifying uranium-234 from aged plutonium-238 solutions were investigated at the tracer level. The plutonium was first reduced to the trivalent form (by ferrous sulfate in the first procedure and by hydroxylamine in the second. Then the uranium was eluted from plutonium on Dowex 1X4 anion exchange resin. Plutonium remained on the resin. At the low plutonium concentrations used, difficulty was experienced in accurately counting the plutonium which remained on the resin; however, both methods gave satisfactory separation of uranium-234 from the plutonium solution.

Isotope Separation

Helium-3 Separation and Purification The absolute accuracy for the analysis of tritium in helium-3 by internal geiger counting was checked against a 53.84 atom per cent tritium standard (as determined by mass spectrometry) and found to be within the precision of the method (1.25%).

Since helium-3 does not exhibit the phenomenon of superfluidity below the lambda point, attempts are being made to separate the helium isotopes by use of this principle. Preliminary attempts at separation by filtration were unsuccessful.

Carbon Isotope Separation Carbon monoxide and methane are being evaluated as feed materials for purifying carbon-13 by thermal diffusion. A feed product with 60.86 per cent carbon-13 in the total carbon was purified in two 24-foot concentric-tube columns; the bottom product contained 91.46 per cent carbon-13 in the total carbon.

Three runs were made on the methane purification system. In one run methane was enriched from 99.0 per cent in the feed to 99.9 per cent in the product.

Two runs were made in the thermal decomposition studies using a carbon-sheathed Nichrome V wire. There was a 0.47 and 1.04 per cent decomposition of carbon monoxide.

A 12-foot Nichrome V thermal diffusion column wire was heated by alternating current. As the current increased, the wire vibrated. There was no visible vibration, however, when the wire was heated or cooled rapidly.

A literature search was made to determine methods for predicting equilibrium constants for chemical exchange. Mathematical calculations of these constants were made for simple molecules.

Four different methods were considered for enrichment of carbon-13. The bicarbonate method was cheap and simple; however, the reaction rate was slow. With monoethanolamine and carbon dioxide, separation factors of 1.004, 1.008, and 1.046 were obtained as reported in the literature. In a third method HC^{13}N was formed; toxicity, high cost, and HCN polymerization were disadvantages of this technique. A carbon dioxide-carbon monoxide system had a single-stage separation factor of 1.086; difficulty has been encountered in overcoming the slow reaction rate of this method.

Thermal Diffusion Theory A new theory of the operation of the thermal diffusion column was recently developed. Three equations were written based on the assumption that the column is in a quasi-stationary state and the convective velocity is in the vertical direction only.

The $\Omega^{(2,3)*}(T)$ collision integrals were calculated for the helium potential function from 100° to 2000°K at 100-degree intervals.

Analytical

Beryllium Analysis by Gamma Activation A nondestructive method for determining total beryllium in powdered beryllium samples by gamma activation has been investigated. A standard curve was made, and duplicate analyses on various beryllium samples were determined. The method had a precision of better than ± 0.2 per cent.

ADHESIVES AND PLASTICS RESEARCH

Adhesives

Adhesives formulations are being developed to obtain a system which is compatible with explosives and possesses satisfactory manipulation and curing characteristics. These adhesives must retain flexibility at low temperatures and designed tensile strength at elevated temperatures.

The results of environmental testing of the first casting of 13 adhesive formulations in the Adhesive Evaluation Project reported previously [MLM-1133 and MLM-1136] were for two-week, four-week, and twelve-week old test specimens of ten anhydride-cured Oxiron, and three polyol-cured Adiprene formulations. For evaluation at longer aging periods, it was necessary to make a second casting of each of the same formulations in February, 1962. The results for 26-week old specimens of the second series of casting were reported [MLM-1142], and evaluation for 52-week old specimens was made in March, 1963.

The evaluation results for both 26-week and 52-week old specimens show that little degradation occurred in the six-month period. Because the humidity conditions during the few days preceding the two series of tests were quite different, changes in physical properties of the test specimens were ascribed to aging only.

Further exploratory studies on the application of carbon black-silver combination fillers were made. The results of electrical resistivity and tensile bond strength determination made after two weeks of conditioning at 160°F showed that the use of carbon black in combination with silver fillers not only increased the electrical conductivity, but also improved the bond strength. The tensile bond strength of the carbon black and silver filled Adiprene adhesives varied from 320 to 390 pounds per square inch at room temperature as compared to 100 pounds per square inch for the adhesives filled with silver powders.

Plastics

Mound Laboratory is conducting research on the molding properties of diallyl phthalate in an effort to obtain superior plastic parts for the detonator program.

Five fillers, i.e., a graphite fiber, a graphite foam, a carbon fiber and two silica powders, were incorporated into diallyl phthalate formulations for experimental molding powders in an attempt to improve the existing production materials. Although the graphite and carbon fiber-filled test specimens had tensile strengths and heat distortion temperatures higher than the asbestos-filled materials, the impact strength was not significantly higher than the standard production material. The carbonaceous filled formulations did not have arc resistance, and were unsuitable for use as detonator heads. The moldings filled with graphite foam were soft, and had low tensile strengths.

The silica-filled moldings had the same physical characteristics as the production material. Detonator heads were molded from the five filled formulations and x-rayed by the usual quality control techniques. With the exception of the foam formulations, all the materials would be rejected because of high density inclusions. The foam formulations would be rejected because of cracks.

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-208 and Polonium-209

Polonium-208 and Polonium-209 in Irradiated Bismuth The relative yields of polonium-208 and polonium-209 in reactor produced polonium-210 have been determined again by counting methods, with greater accuracy than previously reported [MLM-1145]. The initial atom ratios of the polonium isotopes (R_{N_0}), normalized to an irradiation period of 100 days, are given in Table 1. The Po^{210}/Po^{209} and Po^{210}/Po^{208} ratios are given to show that it is not possible to obtain significant amounts of the light polonium isotopes by irradiating bismuth in a thermal reactor. The Po^{209}/Po^{208} ratio is close to the value predicted on the basis of a Maxwellian distribution of thermal neutrons: The theoretical value of R_{N_0} for Po^{209}/Po^{208} is 1500, assuming both species are produced by (n, xn) reactions on polonium-210, and assuming a Maxwellian distribution of the neutron flux. [See MLM-1145 for a discussion of the theory.] Threshold energies of 7.71 and 14.96 Mev for the polonium-210 $(n, 2n)$ and polonium-210 $(n, 3n)$ reactions, respectively, were taken from the neutron binding energies tabulated by Cameron [A. G. W. Cameron, "A Revised Semi-Empirical Mass Formula," Canadian Report CRP-690, 1957]. For other types of reactors all the ratios would be expected to be different, depending on the neutron energy distribution.

Table 1

INITIAL ATOM RATIOS OF THE POLONIUM ISOTOPES, NORMALIZED

Sample No.	R_{N_0}		
	Po^{210}/Po^{208}	Po^{210}/Po^{209}	Po^{209}/Po^{208}
1	$(3.9 \pm 1.1) \times 10^{10}$	$(2.73 \pm 0.03) \times 10^9$	$1.4 \pm 0.4 \times 10^3$
2	$(10.8 \pm 2.6) \times 10^{10}$	$(6.04 \pm 0.03) \times 10^9$	$1.8 \pm 0.4 \times 10^3$
3	$(12.0 \pm 3.1) \times 10^{10}$	$(4.21 \pm 0.02) \times 10^9$	$2.9 \pm 0.7 \times 10^3$

The polonium-208 which had been at Argonne National Laboratory was returned. The total activity of polonium in the equipment was about 300 millicuries. The polonium in a one-liter solution, obtained at Argonne National Laboratory when a monel fluorination apparatus was rinsed with acid, has been radiochemically separated. This material contains about 300 microcuries of polonium-208 and about 15 microcuries of polonium-209. This sample will be used for an accurate determination of the half-life of polonium-209. The half-life will be determined by measuring the alpha activity ratio and the mass ratio of the two polonium isotopes. The alpha activity ratio has been determined. Due to experimental difficulty the initial attempt to measure the mass ratio was unsuccessful.

Two new radiochemical procedures have been developed and evaluated for the purification of the polonium in the Argonne Laboratory material. Both methods were successful at the tracer level. In the first method polonium was sorbed onto anion exchange resin from one molar hydrochloric acid while the main impurities (nickel and iron) were rapidly eluted. Polonium was then eluted with one molar phosphoric acid. A disadvantage of this method is that large quantities of polonium destroy the exchange properties of the resin, making it impossible to elute the polonium.

In the second method a cation exchange resin was employed. Polonium was not sorbed significantly onto cation resin from one molar hydrochloric acid while iron and nickel were strongly sorbed. Thus, by loading a mixture of polonium, iron, and nickel onto the cation resin from a solution of one molar hydrochloric acid the polonium can be separated from the other impurities. Further experiments are in progress to evaluate the effectiveness of a cation exchange resin separation of tellurium and polonium.

Polonium-208 and Polonium-209 Decay Schemes The gamma decay schemes of polonium-208 and 209 are being investigated. The coincidence system for the measurement of the decay energies consists of a 256-channel pulse height analyzer, linear amplifiers, a five-channel coincidence circuit and either a two-inch by two-inch NaI(Tl) crystal or a matched pair of three-inch by three-inch NaI(Tl) detectors (resolution less than 8% for Cs¹³⁷ 0.661-Mev line).

A delay line was placed between the amplifier and the analyzer on the main pulse train. The fast-slow coincidence circuit furnished a gate pulse to the analyzer to satisfy coincidence conditions; however, about 2.3 microseconds were required for conclusive analysis when both fast and slow circuits were used. The slow circuit was used to impose an amplitude restriction by means of a single channel analyzer; thus, the main pulse train was delayed about 3.0 microseconds in order to permit the gate pulse to arrive at the analyzer first.

Either leading edge or zero transition coincidence analyses using the trailing edge of pulses were possible in the coincidence circuit. The trailing edge mode reputedly permitted the use of minimal resolving times. Studies with Hamner amplifiers, however, indicated that more satisfactory results were attained with a low discrimination trigger for the input pulses with a leading edge mode of analysis.

The cobalt-60 spectrum was used as a guide in the choice of coincidence parameters. The 1.17- and 1.33-Mev gamma rays from this nuclide are in prompt coincidence. Thus, coincidence spectra were readily attained by adjusting the single channel analyzer in one of the channels of the coincidence system to encompass one or the other of these peaks and gating the multichannel analyzer with the resulting coincidence pulses. Figure 1 shows both gross (single) spectrum of cobalt-60 and a coincidence spectrum obtained by gating on the 1.33-Mev peak. The apparent shift of channel numbers of the 1.17-Mev peak was due to analyzer problems which have since been eliminated.

It was important to maintain counting rates at reasonable values to minimize accidental coincidences and prevent distortion of spectral shape. Measurements are currently being made at counting rates no greater than 5×10^5 counts per minute per detector.

Single gamma-ray spectra obtained from sources having different amounts of polonium-208 and polonium-209 are shown in Figures 2 and 3. These spectra were obtained with two-inch by two-inch NaI(Tl) detectors. Prominent energies were displayed at 75 kev, 130 to 140 kev, 260 kev, 580 kev, and 900 kev. The 75-kev peak was characteristic of x-ray spectra from polonium; contributions to peaks of this type include internal conversions or electron captures.

The source used for obtaining the spectrum shown in Figure 3 contained a substantially smaller amount of polonium-208 than in the source shown in Figure 2. The broad peak at 570 kev was absent in this case. The peaks at 900 and 260 kev were quite prominent and in a comparable ratio to the same peaks in Figure 2. A peak at about 130 kev was evident. The broadening on the low energy side of the 900-kev peak was due to

Figure 1. Single and Coincidence Spectra of Cobalt-60.

Figure 2. Polonium-208/Polonium-209 Single Gamma-ray Spectrum.

residual contamination from polonium-210, which has no other gamma rays which would interfere with the polonium-208-polonium-209 spectra and may thus be independently accounted for.

Coincidence spectra were measured gating on all the main photopeaks described above. Coincidences existed between two separate states in the vicinity of the 570-kev peak and a corresponding pair of states around the 260-kev peak. There was evidence that each of these transitions was delayed by a different amount of time. These were thought to arise from electron capture decay in polonium-208 since there was evidence that the x-ray was also part of the overall transition. The main contribution to the peak in the single spectrum came from yet another state, probably alpha decay in polonium-209. There also appeared to be delayed coincidences between the x-ray and the 900-kev state, apparently due mainly to polonium-209. The assignment of the 140-kev state was uncertain.

Figure 3. Polonium-208/Polonium-209 Single Gamma-ray Spectrum.

Delayed coincidence data did not agree satisfactorily, probably due to uncertainty in the time alignment of the two coincidence channels using a leading edge pulse trigger. New double delay line amplifiers have well-defined zero crossover points on the trailing edge and should be more uniform in time. These will be employed in connection with the 800-channel analyzer since the 10-volt output pulse is insufficient for the 256-channel system.

Disposal of Polonium Process Waste

The decontamination factors obtained with various treatments of wastes from the polonium process were investigated. Samples of a typical waste solution were treated by precipitation of various metal hydroxides at different pH levels. The alpha, beta, and gamma activities were measured and compared with the activity of the original solution.

In the first series of runs the decontamination was measured as a function of the pH at which precipitation occurred, without the addition of any other reagents. In this case, aluminum hydroxide (from the aluminum jacket) and bismuth hydroxide (from the slug) precipitated. The results are given in Table 2. A decontamination factor of 4000 would be required to bring the activity of these samples to a level which would not require further waste disposal treatment.

Table 2

**DECONTAMINATION OF POLONIUM PROCESS SOLUTIONS BY
HYDROXIDE PRECIPITATION - NO ADDED REAGENTS**

pH of Precipitation	Decontamination Factor		
	Alpha Count	Beta Count	Gamma Count
5.0	380	110	23
7.0	410	130	33
8.0	485	180	58
10.0	360	160	82
12.0	255	105	39

A second series of experiments was carried out in which various reagents were added to the original sample before the pH was adjusted to precipitate the hydroxides. The data are summarized in Table 3. The decontamination factor was not high enough in any case to preclude further treatment. It was concluded that a single treatment of polonium process wastes will not lower the activity to an acceptable level.

Table 3

**DECONTAMINATION OF POLONIUM PROCESS
SOLUTIONS BY HYDROXIDE PRECIPITATION**

pH of Precipitation	Reagent Added	Decontamination Factor		
		Alpha Count	Beta Count	Gamma Count
8.0	Fe	161	235	481
8.0	Ba	377	143	30
8.0	Fe + Ba	128	217	308
8.0	Fe + Ca	426	240	70
8.0	Fe + Ba + Ca	240	221	118
10.0	Fe	452	260	194
10.0	Fe + Ba	292	242	265

Further tests were carried out using two successive hydroxide precipitations. A typical polonium process waste batch (HH-17) was used for these experiments. Alpha, beta, and gamma counts were obtained as before. Included in this series of experiments were the results of the plant treatment: First bismuth hydroxide was precipitated at pH 12 (the filtrate from this step is identified in Table 4 as F₁ and HH-17AT). After removal of the bismuth hydroxide by filtration, 50 pounds of ferric sulfate were added to the solution then ferric hydroxide was precipitated by adding sodium hydroxide until the pH of the mixture was 7.5 (the filtrate from this step is identified in Table 4 as F₂ and F₂S). The filtrate from the first precipitation was treated further in laboratory tests (Table 5).

Table 4

DECONTAMINATION OBTAINED ON PLANT TREATMENT OF BATCH HH-17

Sample and Treatment	(Counts/min/ml)			Decontamination Factor		
	Alpha	Beta	Gamma	Alpha	Beta	Gamma
HH-17 (original)	26.63×10^4	6.002×10^4	120,209	--	--	--
F ₁ (centrifuged)	900	5,100	910.3	29,590	1,117	132
HH-17AT (filtrate)	7,000	24,000	9,533	3,804	250	12.6
F ₂ (centrifuged)	300	3,000	24.7	88,400	2,000	4,875
F ₂ S (filtrate)	600	3,800	30.0	44,400	1,579	4,009

Table 5

DECONTAMINATION OF HH-17 BY TREATMENT OF FIRST FILTRATE (F₁)

Sample and Treatment	(Counts/min/ml)			Decontamination Factor		
	Alpha	Beta	Gamma	Alpha	Beta	Gamma
HH-17 (original)	26.63×10^4	6.002×10^4	120,209	--	--	--
F ₁ , Fe, pH6	200	5,500	548.8	130,000	1,091	219
F ₁ , Fe, pH6, no Celite	60	4,700	777.9	442,000	1,277	154
F ₁ , Fe, pH7	--	--	654.1	--	--	184
F ₁ T (Fe, pH7.5)	100	4,200	174.5	266,000	1,429	689
F ₁ , Fe, pH8	--	--	138.1	--	--	870
F ₁ , Fe, pH10	160	3,700	28.2	166,000	1,622	4,266
F ₁ , pH10, Fe, pH10	140	4,400	30.4	190,000	1,364	3,952
F ₁ , Fe + Be, pH10	--	--	25.4	--	--	4,798
F ₂ , 25 lbs Fe,	--	--	19.5	--	--	6,177
50 lbs Fe ₂ (SO ₄) ₃ , pH10						
F ₁ , Carbon, pH8, no Celite	--	--	110.5	--	--	1,102

It should be noted that the original beta count may be high by a factor of two or more due to the extremely high alpha count. The most reliable data are those obtained by gamma counting. In this case, the data indicate that satisfactory activity levels would be obtained with a decontamination factor of 4000. Thus, any of the second precipitations with iron at pH 10 would be useful. Further tests will determine the effect of decreasing the amount of ferric sulfate in the mixture.

Actinium-227

Heat Source Application The feasibility of using actinium-227 as a radioactive heat source material was estimated from production data and the power level available from the decay chain. The maximum power density for actinium-227 is about 15 watts per gram, and the power level is 14 watts per gram or greater in the period from 85 days to 1000 days. The unshielded gamma radiation at equilibrium is 1.71 roentgens per hour at one meter per watt with maximum gamma energy of 0.83 Mev.

The chief drawback to the use of actinium-227 is the limited supply of radium-226 that can be irradiated. Because of the high thermal neutron cross section of actinium-227, the maximum actinium-227 yield from radium-226 irradiation is about 2.3 per cent. With this yield the radium burnup is high.

Half-life Studies The half-life of actinium-227 was previously given as 21.7708 years, with an internal probable error of 0.0018 year [MLM-1145]. The data were solved by the double variational method for radium-226 and thorium-228 content. The growth curves were also solved for the half-life of thorium-227. For sample Z-18 (Table 6) the half-life result was 18.729 ± 0.048 days [MLM-1151]. The results were 18.47 days for Z-14 with three measurements—therefore, no probable error could be calculated—and 18.60 ± 0.15 days for Z-13 with only five measurements. From these analyses, absolute probable errors were assigned, and the grand mean half-life of actinium-227 was recalculated. The final result was 21.7714 (+0.0056, -0.0033) years. The plus limits were based on the possible thorium-228 content, and the minus limits were based on radium-226. Originally the actinium-227 was produced in pile irradiated radium-226 samples, and because of the high neutron cross section of actinium-227, large amounts of thorium-228 were also produced.

Table 6

**REGRESSION LINES OF THORIUM-228 AND RADIUM-226
ACTIVITY VERSUS THE HALF-LIFE OF ACTINIUM**

Sample	Calorimeter	Thorium-228 Activity (microwatts)	Radium-226 Activity (microwatts)
Z-13	39	1550.3 ($T_{1/2}$ -21.7696)	5267.4 (21.7723 - $T_{1/2}$)
Z-13	51	2405.0 ($T_{1/2}$ -21.7759)	5383.9 (21.7767 - $T_{1/2}$)
Z-14	39	727.3 ($T_{1/2}$ -21.7759)	2532.4 (21.7767 - $T_{1/2}$)
Z-18	51	1240.8 ($T_{1/2}$ -21.7354)	2935.8 (21.7401 - $T_{1/2}$)

The data were used as the limiting factor for the values of the thorium-228 content and plus probable errors. The weight of the samples compared to the calculated weight was the primary limiting factor for the radium-226 content and minus probable errors.

For reference purposes, a partial table of actinium-227 half-life determinations is shown in Table 7 [MLM-1145].

Table 7

**ACTINIUM-227 HALF-LIFE DETERMINATIONS
ASSUMING A SINGLE EXPONENTIAL DECAY SCHEME**

Sample Designation	Calorimeter	Half-Life (yrs)	Internal Probable Error (yrs)
X-13	39	21.7721	0.0022
X-13	51	21.7726	0.0058
X-14	39	21.7766	0.0045
X-14	51	21.7628	0.0066
X-18	51	21.7397	0.0083

Table 6 gives the regression lines of thorium-228 and radium-226 versus the half-life of actinium-227. The regression lines give the most probable relationship between the constants. (The lines are very straight over the range of a few probable errors.) For example, if there were 100 microwatts of thermal activity of radium-226 in sample Z-13, the half-life of actinium-227 would be: $21.7723 - (100/5267.4) = 21.7533$ years, instead of 21.7723 years. Alternately, if the half-life of actinium-227 is 21.7714 years, then Z-18 contains $1240.8 - (21.7714 - 21.7354) = 45$ microwatts of thorium-228. An unresolved problem of the regression lines is that the half-life of actinium-227, corresponding to no radium-226 or thorium-228 at zero value of a regression line, is slightly different from the half-life of actinium-227 obtained assuming no radium-226 or thorium-228 to start with, as can be seen from comparing Tables 6 and 7. This occurs in all similar situations, and it is not known which result is more valid. At present, the results used are from the values in Table 7 for the grand mean calculations.

Table 8 gives the least squares solutions when solving for three unknowns: the initial quantities of actinium-227 and thorium-228 and the half-life of actinium-227. The half-life of thorium-228 was assumed to be 1.9 years. The probable errors in the half-life of actinium-227 have increased by a factor of three because of the additional unknown, as can be seen by comparing Table 8 to Table 7. However, the increase in probable error has meaning only if it does not signify a negative amount of thorium-228, and this can be determined by means of the regression lines of Table 6. Approximate limits on the possible thorium-228 content have been estimated from the growth curves. The power-time curve of actinium-227 reaches a peak at 185 days and is about 380 times greater than the initial power. The low level of power can initially be used to set small limits on other radioactive isotopes. The limits in Table 8, however, are not as small as the limits that are established by the probable errors in the half-life of actinium-227. For instance, Table 8 gives a probable error of 0.0069 day for one half-life measurement which, combined with the corresponding regression line of Table 6, gives a probable error limit of $1550.3 \times 0.0069 = 10.7$ microwatts for the thorium-228 content. For this reason the plus limits for the half-life of actinium-227 in Table 8 were used in calculating the grand mean and plus internal probable errors.

Table 8

**LEAST SQUARES SOLUTIONS AND PROBABLE ERRORS FOR
HALF-LIFE AND ACTIVITY OF ACTINIUM-227 AND ACTIVITY OF THORIUM-228**

Sample	Calorimeter	Half-life and Probable Error of Ac ²²⁷ (yrs)	Initial Th ²²⁸ Activity (microwatts)	Limit of Th ²²⁸ From Growth Curves (microwatts)
Z-13	39	21.7953 ± 0.0069	39.9	120
Z-13	51	21.7341 ± 0.0210	-100.5	120
Z-14	39	21.7826 ± 0.0143	4.9	60
Z-18	51	21.8000 ± 0.0319	80.2	70

Table 9 gives the corresponding results when the data are solved for possible radium-226 content. There would be a problem if limits were not set either by the gram weights of the samples or from the growth curves. The minus probable error values were chosen according to the smallest of the three limits. The probable errors in the half-lives were too high to be the controlling factor. The weights were the limits in the first three cases and the growth curves in the last case. These limits were substituted in the regression lines

of Table 6 and the variations in the half-lives ($\Delta T_{1/2}$) were calculated. These $\Delta T_{1/2}$ values were then combined with the probable errors of Table 7 to give the minus probable errors according to the equation:

$$[(\Delta T_{1/2})^2 + (\text{P.E.})^2]^{1/2} = \text{Probable Error (Minus)}$$

Table 9

**LEAST SQUARES SOLUTIONS AND PROBABLE ERRORS FOR
HALF-LIFE AND AND ACTIVITY OF ACTINIUM-227 AND ACTIVITY OF RADIUM-226**

Sample	Calorimeter	Half-Life and Probable Error of Ac ²²⁷ (yrs)	Initial Ra ²²⁶ Activity (microwatts)	Limit of Ra ²²⁶ By Weight (microwatts)	Limit of Ra ²²⁶ From Growth Curves (microwatts)
Z-13	39	21.4867 ± 0.0629	1504.9	18	120
Z-13	51	22.0915 ± 0.0204	-1718.7	18	120
Z-14	39	21.6589 ± 0.1358	298.3	32	60
Z-18	51	21.1895 ± 0.2780	1616.6	168	70

Final results for each set of data are given in Table 10. The probable error of Z-14 in calorimeter 51 was estimated.

Table 10

HALF-LIVES OF ACTINIUM-227

Sample	Calorimeter	Half-Life (yrs)	Absolute Probable Errors (yrs)
Z-13	39	21.7721	$\left\{ \begin{array}{l} + 0.0069 \\ - 0.0040 \end{array} \right.$
Z-13	51	21.7726	$\left\{ \begin{array}{l} + 0.0210 \\ - 0.0067 \end{array} \right.$
Z-14	39	21.7766	$\left\{ \begin{array}{l} + 0.0143 \\ - 0.0133 \end{array} \right.$
Z-14	51	21.7628	$\left\{ \begin{array}{l} \text{Estimated} \\ \pm 0.0205 \end{array} \right.$
Z-18	51	21.7397	$\left\{ \begin{array}{l} + 0.0319 \\ - 0.0253 \end{array} \right.$

The grand mean was calculated for both the plus and the minus limits in Table 10, and the average was taken as the best value. Table 11 gives the results. The probable errors from internal consistency were used for

final results since they are over twice as large as the probable errors from external consistencies. It is quite obvious that the errors due to internal consistencies should be used because the external probable errors decrease when the probable error of each half-life increases, i.e., as the degree of confidence in each individual half-life measurement decreased, the consistency among the half-lives increased.

Table 11

GRAND MEAN HALF-LIFE OF ACTINIUM-227 WITH PROBABLE ERRORS

Limits	Grand Mean Half-Life (yrs)	Internal Consistency (yrs)	External Consistency (yrs)
Plus	21.7711	+ 0.0056	0.0022
Minus	21.7717	- 0.0033	- 0.0016

$$\text{Average} = 21.7714 \begin{array}{l} + 0.0056 \\ - 0.0033 \end{array} \text{ yrs}$$

Actinium-227 half-life calculations are now complete. Analyses from many points of view have produced no evidence of radioactive impurities, chemical effects, and shifts in the calorimeters and measuring equipment during the ten years covered by the measurements.

Growth Constants In last month's report, the equations describing the growth of the principal alpha-emitters in the actinium-227 decay chain were given. Recalculation of the equations was necessary to take into account the new half-life values of actinium-227, thorium-227, and radium-223 as recently determined at Mound Laboratory.

Tables 12 through 17 give the numerical values of the growth and decay factors for various periods of time. These tables supersede their counterparts in the previously published "Decay and Growth Tables for the Naturally Occurring Radioactive Series" [H. W. Kirby, *Anal. Chem.*, 26, 1063 (1954).].

Table 12

DECAY OF PURE RADIOISOTOPE

Time (min)	Th ²²⁷	Ra ²²³	Time (min)	Th ²²⁷	Ra ²²³
1	.99997429	.99995790	31	.99920358	.99869580
2	.99994859	.99991580	32	.99917790	.99865376
3	.99992290	.99987371	33	.99915223	.99861172
4	.99989720	.99983162	34	.99912655	.99856968
5	.99987150	.99978953	35	.99910087	.99852764
6	.99984580	.99974744	36	.99907519	.99848560
7	.99982011	.99970535	37	.99904951	.99844357
8	.99979441	.99966327	38	.99902384	.99840154
9	.99976871	.99962118	39	.99899816	.99835951
10	.99974302	.99957910	40	.99897249	.99831748
11	.99971733	.99953702	41	.99894681	.99827545
12	.99969163	.99949494	42	.99892114	.99823343
13	.99966594	.99945287	43	.99889547	.99819140
14	.99964025	.99941079	44	.99886979	.99814938
15	.99961456	.99936872	45	.99884412	.99810736
16	.99958887	.99932665	46	.99881845	.99806535
17	.99956318	.99928458	47	.99879278	.99802333
18	.99953749	.99924251	48	.99876711	.99798132
19	.99951180	.99920045	49	.99874144	.99793930
20	.99948611	.99915838	50	.99871578	.99789729
21	.99946042	.99911632	51	.99869011	.99785528
22	.99943474	.99907426	52	.99866444	.99781328
23	.99940905	.99903220	53	.99863878	.99777127
24	.99938336	.99899015	54	.99861311	.99772927
25	.99935768	.99894809	55	.99858745	.99768727
26	.99933200	.99890604	56	.99856178	.99764527
27	.99930631	.99886399	57	.99853612	.99760327
28	.99928063	.99882194	58	.99851045	.99756127
29	.99925495	.99877989	59	.99848479	.99751928
30	.99922927	.99873784	60	.99845913	.99747728

Table 13

DECAY OF PURE RADIOISOTOPE

Time (hrs)	Th ²³²	Ra ²²³
1	.99845913	.99747728
2	.99692064	.99496094
3	.99538452	.99245094
4	.99385076	.98994727
5	.99231937	.98744992
6	.99079034	.98495887
7	.98926367	.98247410
8	.98773935	.97999560
9	.98621737	.97752335
10	.98469774	.97505734
11	.98318046	.97259755
12	.98166551	.97014397
13	.98015289	.96769658
14	.97864261	.96525536
15	.97713465	.96282030
16	.97562902	.96039138
17	.97412570	.95796859
18	.97262471	.95555191
19	.97112602	.95314133
20	.96962965	.95073683
21	.96813558	.94833839
22	.96664381	.94594601
23	.96515434	.94355966
24	.96366717	.94117933

DECAY OF PURE RADIOISOTOPE

Time (days)	Ac ²²⁷	Th ²²⁷	Ra ²²³
1	.99991283	.96366717	.94117933
2	.99982568	.92865442	.88581853
3	.99973853	.89491378	.83371410
4	.99965139	.86239903	.78467448
5	.99956426	.83106563	.73851939
6	.99947714	.80087067	.69507919
7	.99939002	.77177277	.65419417
8	.99930291	.74373209	.61571403
9	.99921581	.71671020	.57949732
10	.99912872	.69067009	.54541090
11	.99904163	.66557609	.51332946
12	.99895455	.64139383	.48313508
13	.99886748	.61809018	.45471676
14	.99878042	.59563322	.42797001
15	.99869336	.57399218	.40279653
16	.99860632	.55313742	.37910377
17	.99851927	.53304037	.35680466
18	.99843224	.51367351	.33581717
19	.99834522	.49501030	.31606417
20	.99825820	.47702518	.29747306
21	.99817119	.45969350	.27997549
22	.99808419	.44299154	.26350714
23	.99799719	.42689640	.24800749
24	.99791020	.41138605	.23341952
25	.99782322	.39643923	.21968963
26	.99773625	.38203547	.20676733
27	.99764929	.36815504	.19460513
28	.99756233	.35477893	.18315835
29	.99747538	.34188881	.17238485
30	.99738844	.32946702	.16224505
31	.99730150	.31749655	.15270169
32	.99721458	.30596101	.14371967
33	.99712766	.29484458	.13526598
34	.99704075	.28413204	.12730955
35	.99695384	.27380872	.11982112
36	.99686694	.26386048	.11277316
37	.99678006	.25427368	.10613976
38	.99669317	.24503520	.09989655
39	.99660630	.23613238	.09402057
40	.99651943	.22755302	.08849022
41	.99643258	.21928537	.08328516
42	.99634572	.21131812	.07838627
43	.99625888	.20364033	.07377554
44	.99617205	.19624150	.06943601
45	.99608522	.18911149	.06535174
46	.99599840	.18224054	.06150771
47	.99591158	.17561922	.05788978
48	.99582478	.16923848	.05448467
49	.99573798	.16308957	.05127984
50	.99565119	.15716406	.04826352

Table 14 (cont.)

Time (days)	Ac ²²⁷	Th ²²⁷	Ra ²²³
51	.99556441	.15145385	.04542463
52	.99547763	.14595110	.04275273
53	.99539086	.14064829	.04023798
54	.99530410	.13553814	.03787116
55	.99521735	.13061365	.03564355
56	.99513060	.12586809	.03354697
57	.99504387	.12129494	.03157372
58	.99495714	.11688796	.02971653
59	.99487041	.11264109	.02796858
60	.99478370	.10854852	.02632345
61	.99469699	.10460464	.02477509
62	.99461029	.10080406	.02331780
63	.99452360	.09714156	.02194623
64	.99443691	.09361214	.02065534
65	.99435024	.09021094	.01944038
66	.99426357	.08693332	.01829688
67	.99417691	.08377479	.01722065
68	.99409025	.08073101	.01620772
69	.99400361	.07779783	.01525437
70	.99391697	.07497121	.01435709
71	.99383033	.07224730	.01351260
72	.99374371	.06962235	.01271778
73	.99365709	.06709277	.01196971
74	.99357048	.06465510	.01126565
75	.99348388	.06230600	.01060299
76	.99339729	.06004224	.00997932
77	.99331070	.05786074	.00939233
78	.99322412	.05575850	.00883986
79	.99313755	.05373263	.00831990
80	.99305099	.05178037	.00783051
81	.99296443	.04989905	.00736992
82	.99287788	.04808607	.00693641
83	.99279134	.04633897	.00652841
84	.99270481	.04465534	.00614440
85	.99261828	.04303289	.00578299
86	.99253176	.04146938	.00544283
87	.99244525	.03996268	.00512267
88	.99235875	.03851072	.00482136
89	.99227225	.03711152	.00453776
90	.99218576	.03576315	.00427085
91	.99209928	.03446378	.00401963
92	.99201281	.03321161	.00378319
93	.99192634	.03200494	.00356066
94	.99183989	.03084211	.00335122
95	.99175343	.02972153	.00315410
96	.99166699	.02864166	.00296857
97	.99158056	.02760103	.00279396
98	.99149413	.02659820	.00262962
99	.99140771	.02563182	.00247494
100	.99132129	.02470054	.00232936
150	.98701023	.00388203	.00011242
200	.98271791	.00061011	.00000542
250	.97844426	.00009588	.00000026
300	.97418920	.00001507	.00000001
350	.96995264	.00000236	0.00000000
365	.96868526	.00000135	0.00000000

Table 15

GROWTH OF ALPHA ACTIVITY FROM INITIALLY PURE ACTINIUM-227

Time (hrs)	Relative alpha	Time (hrs)	Relative alpha	Time (hrs)	Relative alpha
1	.01357	41	.08927	81	.18183
2	.01522	42	.09139	82	.18433
3	.01689	43	.09353	83	.18684
4	.01858	44	.09567	84	.18936
5	.02027	45	.09782	85	.19189
6	.02198	46	.09999	86	.19443
7	.02371	47	.10216	87	.19697
8	.02544	48	.10434	88	.19953
9	.02719	49	.10654	89	.20209
10	.02895	50	.10874	90	.20466
11	.03072	51	.11096	91	.20724
12	.03251	52	.11318	92	.20982
13	.03430	53	.11542	93	.21241
14	.03611	54	.11766	94	.21502
15	.03793	55	.11992	95	.21763
16	.03976	56	.12218	96	.22025
17	.04161	57	.12445	97	.22287
18	.04346	58	.12674	98	.22551
19	.04533	59	.12903	99	.22815
20	.04721	60	.13133	100	.23080
21	.04910	61	.13365	101	.23345
22	.05100	62	.13597	102	.23612
23	.05292	63	.13830	103	.23879
24	.05484	64	.14064	104	.24147
25	.05678	65	.14299	105	.24416
26	.05873	66	.14535	106	.24686
27	.06068	67	.14772	107	.24956
28	.06266	68	.15010	108	.25227
29	.06464	69	.15248	109	.25499
30	.06663	70	.15488	110	.25771
31	.06863	71	.15729	111	.26045
32	.07065	72	.15970	112	.26319
33	.07267	73	.16212	113	.26593
34	.07471	74	.16456	114	.26869
35	.07676	75	.16700	115	.27145
36	.07882	76	.16945	116	.27422
37	.08089	77	.17191	117	.27700
38	.08297	78	.17438	118	.27978
39	.08506	79	.17685	119	.28257
40	.08716	80	.17934	120	.28537

Table 16

GROWTH OF DECAY PRODUCTS FROM INITIALLY PURE ACTINIUM-227

Time (days)	Th ²²⁷	Ra ²²³	Relative alpha
0	.00000	.00000	.01200
1	.03589	.00176	.05484
2	.07048	.00551	.10434
3	.10381	.01103	.15970
4	.13592	.01815	.22025
5	.16686	.02671	.28537
6	.19668	.03655	.35450
7	.22541	.04753	.42712
8	.25310	.05953	.50275
9	.27977	.07242	.58094
10	.30547	.08609	.66129
11	.33024	.10044	.74343
12	.35410	.11537	.82701
13	.37709	.13081	.91172
14	.39924	.14666	.99728
15	.42059	.16286	1.08341
16	.44116	.17934	1.16988
17	.46097	.19604	1.25648
18	.48007	.21290	1.34301
19	.49846	.22987	1.42928
20	.51619	.24690	1.51513
21	.53327	.26396	1.60043
22	.54972	.28099	1.68503
23	.56557	.29798	1.76883
24	.58085	.31488	1.85171
25	.59557	.33167	1.93359
26	.60974	.34832	2.01437
27	.62340	.36481	2.09400
28	.63656	.38112	2.17240
29	.64924	.39723	2.24952
30	.66146	.41312	2.32531
31	.67323	.42878	2.39974
32	.68457	.44420	2.47277
33	.69549	.45937	2.54438
34	.70601	.47428	2.61454
35	.71615	.48892	2.68324
36	.72592	.50328	2.75046
37	.73532	.51736	2.81620
38	.74439	.53115	2.88045
39	.75312	.54466	2.94322
40	.76153	.55788	3.00451
41	.76963	.57080	3.06432
42	.77743	.58343	3.12266
43	.78495	.59577	3.17954
44	.79219	.60782	3.23498
45	.79917	.61958	3.28900
46	.80589	.63104	3.34159
47	.81236	.64222	3.39280
48	.81859	.65312	3.44263
49	.82459	.66374	3.49110
50	.83038	.67407	3.53824

Table 16 (cont.)

Time (days)	Th ²²⁷	Ra ²²³	Relative Alpha λ
51	.83595	.68414	3.58408
52	.84131	.69393	3.62862
53	.84647	.70345	3.67190
54	.85145	.71272	3.71394
55	.85624	.72172	3.75476
56	.86085	.73048	3.79439
57	.86530	.73898	3.83286
58	.86958	.74724	3.87019
59	.87370	.75526	3.90640
60	.87766	.76305	3.94152
61	.88148	.77061	3.97558
62	.88516	.77794	4.00860
63	.88870	.78506	4.04061
64	.89211	.79196	4.07163
65	.89539	.79865	4.10168
66	.89855	.80513	4.13080
67	.90160	.81142	4.15900
68	.90452	.81752	4.18630
69	.90734	.82342	4.21274
70	.91006	.82914	4.23834
71	.91267	.83468	4.26312
72	.91518	.84004	4.28709
73	.91760	.84524	4.31029
74	.91993	.85026	4.33273
75	.92217	.85513	4.35444
76	.92433	.85984	4.37544
77	.92640	.86439	4.39575
78	.92840	.86880	4.41538
79	.93032	.87307	4.43436
80	.93217	.87719	4.45271
81	.93394	.88118	4.47044
82	.93565	.88503	4.48758
83	.93730	.88876	4.50413
84	.93888	.89236	4.52013
85	.94040	.89585	4.53559
86	.94186	.89921	4.55051
87	.94327	.90246	4.56493
88	.94462	.90560	4.57885
89	.94592	.90864	4.59229
90	.94717	.91157	4.60526
91	.94837	.91440	4.61779
92	.94953	.91713	4.62988
93	.95064	.91977	4.64154
94	.95170	.92232	4.65280
95	.95273	.92478	4.66367
96	.95371	.92715	4.67415
97	.95466	.92944	4.68425
98	.95556	.93165	4.69400
99	.95643	.93378	4.70341
100	.95727	.93584	4.71247

Table 17

GROWTH OF DECAY PRODUCTS FROM INITIALLY PURE THORIUM-227

Time (days)	Ra ²²³	Relative alpha
0	.00000	1.00000
1	.05773	1.19248
2	.10997	1.36663
3	.15712	1.52167
4	.19954	1.65903
5	.23760	1.78007
6	.27160	1.88605
7	.30186	1.97814
8	.32867	2.05743
9	.35227	2.12496
10	.37293	2.18166
11	.39087	2.22842
12	.40630	2.26607
13	.41944	2.29538
14	.43045	2.31706
15	.43952	2.33176
16	.44680	2.34012
17	.45246	2.34270
18	.45662	2.34003
19	.45942	2.33261
20	.46097	2.32089
21	.46140	2.30531
22	.46080	2.28624
23	.45927	2.26407
24	.45690	2.23911
25	.45378	2.21170
26	.44997	2.18210
27	.44556	2.15060
28	.44061	2.11743
29	.43518	2.08282
30	.42932	2.04698
31	.42309	2.01010
32	.41653	1.97235
33	.40969	1.93390
34	.40262	1.89489
35	.39534	1.85546
36	.38789	1.81574
37	.38031	1.77582
38	.37262	1.73583
39	.36485	1.69585
40	.35702	1.65596
41	.34916	1.61624
42	.34128	1.57676
43	.33341	1.53758
44	.32555	1.49877
45	.31773	1.46036
46	.30996	1.42240
47	.30225	1.38493
48	.29461	1.34799
49	.28705	1.31160
50	.27958	1.27580

Table 17 (cont.)

Time (days)	$R\alpha^{223}$	Relative alpha
51	.27221	1.24060
52	.26494	1.20602
53	.25779	1.17208
54	.25074	1.13879
55	.24382	1.10617
56	.23702	1.07421
57	.23034	1.04294
58	.22380	1.01234
59	.21738	.98243
60	.21110	.95319
61	.20495	.92464
62	.19893	.89677
63	.19305	.86958
64	.18730	.84306
65	.18169	.81720
66	.17621	.79200
67	.17086	.76745
68	.16565	.74355
69	.16057	.72028
70	.15561	.69763
71	.15079	.67560
72	.14609	.65418
73	.14152	.63335
74	.13707	.61310
75	.13274	.59343
76	.12853	.57432
77	.12443	.55576
78	.12045	.53774
79	.11659	.52024
80	.11283	.50326
81	.10918	.48679
82	.10564	.47080
83	.10220	.45530
84	.09887	.44027
85	.09563	.42569
86	.09249	.41156
87	.08944	.39786
88	.08649	.38459
89	.08362	.37173
90	.08085	.35927
91	.07816	.34721
92	.07555	.33552
93	.07302	.32420
94	.07057	.31325
95	.06820	.30264
96	.06591	.29237
97	.06368	.28244
98	.06153	.27282
99	.05945	.26352
100	.05743	.25451

Residue Adsorption In last month's report, the desorption and separation of protactinium-231, actinium-227, thorium-227, and radium-223 by various reagents and reagent concentrations were discussed. It was pointed out that in the case of the actinium equilibrium mixture (AEM) the gross percentages of radioactivity desorbed were relatively meaningless, inasmuch as the individual radioisotopes of the mixture (Ac^{227} , Th^{227} , Ra^{223} , and the short-lived decay products) exhibit different chemical behavior even at the submicrogram level.

Because of the complex alpha spectrum of AEM (Figure 4) and the low branching ratio (1.2%) and energy (4.94 Mev) of the actinium-227 alpha particle, alpha pulse height analysis is unsatisfactory for the direct quantitative determination of the three principal radioisotopes in AEM. Gamma spectrometry, which can provide semiquantitative data about the behavior of radium-223 and thorium-227, is useless for the quantification of actinium-227. The method of differential decay, based on the growth and decay of the gross alpha activity in a nonequilibrium sample, is more time consuming but produces data with a precision limited only by the precision of the proportional alpha counter. The following method was used for the determination:

Four stainless steel disks were cleaned and masked as previously described. A sample of AEM, consisting of 0.1 microcurie of actinium-227 (0.5 microcurie of alpha activity) in 0.1 ml of 1 N HNO_3 , was transferred to one of the disks, and the micropipet was rinsed with 0.15 ml of distilled water, which was added to the mount. The solution was evaporated to dryness at 90°C , and 0.5 ml of previously boiled and cooled water was added. The solution was again evaporated to dryness at 90°C , and the residue was heated for an additional 5 minutes after the last visible trace of moisture had disappeared.

The residue was covered with 0.5 ml of previously boiled and cooled distilled water and heated for two minutes at 90°C . The solution was transferred to a second disk, and the leaching was repeated.

The residue on the first disk was leached twice with 0.5-ml portions of 0.01 N HNO_3 , and the leachings were transferred to a third disk.

The residue on the first disk was again leached twice with 0.5-ml portions of 0.1N HNO_3 , and the leachings were transferred to a fourth disk.

All four disks were dried at 90°C , and their residues were covered with 0.1 N HNO_3 , and one drop of concentrated NH_4OH . The solutions were dried at 90°C , and the disks were heated to 200°C to drive off the NH_4NO_3 residues. The disks were ignited at red heat in the flame of a Meker burner.

The ignited fractions were alpha-counted periodically over a period of 13 days, and the counting data were analyzed by the method of differential decay. The results (Table 18) are expressed as percentages based on the counting rate of a standard sample of AEM.

Figure 4. Alpha Spectrum of Actinium-227 Equilibrium Mixture.

Table 18

**SEPARATION OF Ac^{227} , Th^{227} , AND Ra^{223} NITRATES BY DESORPTION
IN HNO_3 FROM A STAINLESS STEEL SUBSTRATE**

HNO_3 (N)	Amount Transferred (%)		
	Ac^{227}	Th^{227}	Ra^{223}
0.00	12.6	2.7	85.9
0.01	80.6	80.7	9.7
0.1	0.9	11.4	0.3
Total transferred	94.1	94.8	95.9
Residual	0.5	7.5	2.4
Material balance	94.6	102.3	98.3

The same procedure was followed with hydrofluoric acid as the leaching agent, except that platinum was used as the substrate and the initial residue of AEM was converted to a fluoride before the leaching was carried out.

After the AEM had been mounted, dried, covered with distilled water, and dried again, the residue was covered with 0.5 ml of 0.1 N HF, dried at 90°C, covered with distilled water, dried again and heated for an additional five minutes at 90°C.

The platinum disk was leached successively with two 0.5 ml portions of water, 0.01 N HF, and 0.1 N HF. The three concentrations of leaching agents were transferred to separate stainless steel disks, which were then treated with NH_4NO_3 as above, and ignited at red heat.

The ignited fractions were alpha-counted periodically for 12 days, and the data were analyzed by the method of differential decay. The results are shown in Table 19.

Table 19

**SEPARATION OF Ac^{227} , Th^{227} , AND Ra^{223} FLUORIDES BY DESORPTION
IN HF FROM A PLATINUM SUBSTRATE**

HF (N)	Amount Transferred (%)		
	Ac^{227}	Th^{227}	Ra^{223}
0.00	4.6	0.01	79.0
0.01	3.3	2.6	4.7
0.1	0.4	0.8	2.3
Total transferred	8.3	3.4	86.0
Residual	95.7	99.7	13.5
Material Balance	104.0	103.1	99.5

The results reported in Tables 18 and 19 indicated that a sequential separation of Pa^{231} , Ac^{227} , Th^{227} , and Ra^{223} could be effected by proper selection of reagents.

A sample of protactinium in 0.01 N HF was evaporated to dryness on a gold surface, covered with 0.5 ml of distilled water, and dried again. The residue was covered with 0.25 ml of 2N NH_4OH and again evaporated to dryness.

A sample of AEM in 1 N HNO_3 was deposited on the protactinium residue, dried, covered with distilled water, dried again, covered with 2 N NH_4OH , dried and heated for an additional 5 minutes at 90°C .

The residue was leached twice with 0.5-ml portions of distilled water, and the leachings were transferred to a second gold disk. The residue was then leached twice with 0.5-ml portions of 0.01 N HNO_3 , and the leachings were transferred to a third gold disk.

The residue on the first disk was converted to a fluoride by covering it with 0.5 ml of 0.1 N HF which was evaporated to dryness. The fluoride residue was leached with two 0.5 ml portions of 0.01 N HF , which were transferred to a fourth gold disk.

Alpha pulse height analysis (Figure 5) showed that the actinium-227 and radium-223 separated readily from the protactinium-231. A relatively small fraction of the radium-223 hydroxide was desorbed in water, but essentially all of the actinium-227 and the remainder of the radium-223 were desorbed by 0.01 normal nitric acid. The protactinium-231 moved quantitatively in 0.01 normal hydrofluoric acid, with only a trace of it remaining on the original gold disk (Figure 6 and lowest curve of Figure 5). The thorium-227, however, split into three fractions, part of it moving with the actinium-227 and radium-223 and part with the protactinium-231. A third fraction remained adsorbed on the original surface.

It seems likely that the fractionation of thorium-227 can be prevented by a preliminary group separation with 0.01 normal hydrofluoric acid, which would desorb protactinium-231 and 80 per cent of the radium-223, while leaving the actinium-227 and thorium-227 nearly quantitatively adsorbed. The subsequent separation of protactinium from radium could be accomplished readily with dilute nitric acid. Further work is needed, however, to establish the conditions necessary for the complete separation of actinium and thorium.

An interesting result of the experiment reported above is shown in Figure 6, where the alpha spectra of the original mixture and the separated protactinium are compared. The marked improvement in the resolution of the protactinium alpha peaks after the separation indicates that some nonradioactive debris has been cleared away along with the bulk of the AEM alpha activity, permitting the alpha particles to reach the detector without energy degradation such as is apparent in the lower spectrum of Figure 6.

Thus, the techniques used in residue adsorption appear to be useful for the preparation of alpha sources having improved characteristics as energy and counting standards.

The lower spectrum of Figure 6 also illustrates one of the problems inherent in the use of alpha spectrometry for the quantitative determination of fractionated radioisotopes; unless the physical characteristics of the two sources to be compared are essentially identical, absorption, scattering, and energy degradation of the alpha particles will distort both the heights and the areas of the spectral peaks, yielding inaccurate data.

Figure 5. Separation of Pa^{231} and AEM by Residue Adsorption.

Figure 6. Separation of Pa^{231} and AEM by Residue Adsorption

Further work is needed to improve the separation of protactinium-231 from its decay products and to develop the data needed for the sequential separation of AEM into its three major components.

Uranium-232

The power growth curve for uranium-232 was calculated. If total absorption of alpha and beta emissions from the decay chain is assumed, with no gamma absorption, the power level grows from 0.65 watt per gram of uranium-232 at zero time to a maximum of five watts per gram in approximately 11 years. The power level remains between 4.5 and 5 watts per gram for 5-20 years after chemical purification of the uranium-232.

The gamma radiation growth curve follows the power growth curve very closely after a few days. Radiation intensity per gram of uranium-232 grows from 100 milliroentgens per hour at one meter after 10 days to 18 roentgens per hour at one meter after 11 years. Approximately half of the radiation is from thallium-208.

Uranium-234

Investigations on a tracer level resulted in a proposed scheme to separate and purify uranium-234 from aged plutonium-238 solutions. Uranium is separated from the bulk of the plutonium by anion exchange. Extraction with hexone (methyl isobutyl ketone) further purifies the uranium from plutonium and most other elements. Finally, a TTA (thenoyltrifluoroacetone) extraction removes the last traces of plutonium from the uranium. One batch of feed solution (B-63) was processed according to this method, and a second batch (5H) is in process.

Run 1 - Ferrous Sulfamate Reduction Procedure: Twenty-five ml (0.047 mole) ferrous sulfamate ($\text{Fe}(\text{NH}_4\text{SO}_3)_2$) solution was added to 200 ml 5H feed solution (estimated to contain 5.86 g of plutonium, 0.024 mole). The plutonium was reduced by the ferrous ion according to Equations 1 and 2:

The blue color characteristic of trivalent plutonium appeared as soon as the ferrous solution was added. The solution stood 15 minutes to allow the reaction to go to completion; then 25 ml (0.050 mole) of 2M NaNO_2 was added to destroy half the sulfamic acid and oxidize the trivalent plutonium to tetravalent plutonium (Equations 3 and 4):

Twenty-five ml conc HNO_3 was added to bring the acid concentration to approximately 7.2 N, and the solution was allowed to stand 2 hours before loading onto the column. The final plutonium concentration was 20.89 mg/ml as determined by alpha counting.

Run 1 - Ion Exchange Procedure: A 2.5-cm diameter column containing about 90 ml Dowex 1X4 anion exchange resin was prepared. The resin was previously treated with two acid-base cycles and finally precon-

ditioned with 7.2 N HNO₃. Since the plutonium concentration was relatively high, the solution was loaded slowly with intermittent pauses to allow time for complete absorption. After 163 ml of solution was fed onto the column, the loading was terminated because of excessive gas on the column. The gas resulted from residual sulfamic acid. However, the plutonium remained on the upper half of the column. The column was washed with about one column volume of 7.2 N HNO₃, and the plutonium was eluted with 0.35 N HNO₃. Table 20 gives a summary of the alpha counting data for the resulting solutions from Run 1.

Table 20

PLUTONIUM ANALYSES BY ALPHA COUNTING: RUN 1

Solution	Plutonium Concentration (mg/ml)	Volume (ml)	Total Plutonium (mg)
5H-1 Feed	20.89	163	3400.0
5H-1-1 (Raff.)	0.00004	50	0.002
5H-1-2 (Raff.)	0.00124	50	0.062
5H-1-3 (Raff.)	0.00332	50	0.166
5H-1-4 (Raff.)	0.00507	50	0.25
5H-1-5 (Raff.)	0.00471	28	0.13
5H-1 Pu Elutriate	14.33	220	3150.0

The solutions of Run 1 plus the stripped anion resin were removed separately from the hood line and the 760-kev gamma peak of plutonium-238 was measured with a single channel gamma pulse height analyzer. A sample containing 1.9436 grams of plutonium-238 determined by calorimetry was used as a standard. The counting data and results are given in Table 21. The gamma counting results differed greatly from the alpha counting data, especially at low plutonium concentrations. Since the 760-kev peak is a small fraction of the total gamma spectrum, most of the analysis time is taken with the low energy gamma peaks, and a coincidence correction is needed to compensate for the dead time of the analyzer. Alternatively, an absorber such as a sheet of lead may be placed between the sample and the detector. Since the attenuation of gamma rays is inversely proportional to the energy of the gamma, the unwanted low energy gamma rays will be absorbed to a greater extent than the high energy gamma rays, and the coincidence correction will become less. The only significant conclusion which can be drawn from this data is that the stripped resin had the same order of magnitude of plutonium content as the raffinates, i.e., it contained less than one milligram of plutonium.

Table 21

GAMMA COUNTING OF RUN 1 SOLUTIONS

Sample	Average (cpm)	Calculated Plutonium-238 (mg)	Total Plutonium (mg)
Standard	13,008	1943.6	-
Background	35	5.2	-
5H-1 Feed (112 ml)	7,950	1194.0	2853.0
5H-1-1 (Raff.)	3	0.4	1.0

Table 21 (cont.)

GAMMA COUNTING OF RUN 1 SOLUTIONS

Sample	Average (cpm)	Calculated Plutonium-238 (mg)	Total Plutonium (mg)
5H-I-2 (Raff.)	185	27.6	66.0
5H-I-3 (Raff.)	288	43.0	103.0
5H-I-4 (Raff.)	322	48.1	115.0
5H-I-5 (Raff.)	140	21.0	50.0
Stripped Resin	66	9.9	24.0
5H-I Pu Elutriate	5,717	854.0	2041.0

Run 2 - Hydroxylamine Nitrate Reduction: One hundred ml 5H feed solution (2.93 g, 0.012 mole plutonium) was diluted with distilled water to 400 ml (hydroxylamine reduction is not effective unless the acid concentration is less than 3 N. Fifty ml (0.060 mole) of a 1.2 M solution of hydroxylamine nitrate in 1.2 M HNO₃ was added to reduce the plutonium to the trivalent state [Equations (5) and (6)]:

After the solution stood overnight, 60 ml (0.120 mole) of 2 M NaNO₂ was added to reoxidize the plutonium to the tetravalent state and destroy the excess hydroxylamine [Equations (7) and (8)]:

Two hundred ml of concentrated HNO₃ was added to increase the acid concentration. The final plutonium concentration was estimated to be 3.8 mg/ml as determined by alpha counting; the final calculated acid concentration was 5.6 N rather than the usual 7.2 N.

Run 2 - Loading Procedure: The feed solution 5H-II was loaded on 120 ml of Dowex 1X4 anion exchange resin at 2-4 ml/min. Since the feed was more dilute than in Run 1, it was not necessary to stop the flow to allow time for complete absorption of the plutonium. Three raffinate fractions were collected (see Table 22). About 30 ml resin was loaded. From Run 1, 112 ml of feed solution remained, and this solution was fed to the column. Slower flow rates were used, and it was necessary to stop periodically and allow time for absorption. The plutonium was held on the column satisfactorily; at the end of the loading step about 40 ml of unloaded resin remained at the bottom of the column. Approximately 100 ml 7.2 N HNO₃ was used as wash and was collected with the raffinate (5H-II-4&W). Plutonium was then eluted with 0.35 N HNO₃. To speed up the removal of the last traces of plutonium from the column, a small amount of hydroxylamine nitrate solution was added to the eluting solution. This solution appeared to accelerate the removal of the plutonium as trivalent plutonium, but it produced severe gassing on the column. Analytical results are presented in Table 22.

Table 22

PLUTONIUM ANALYSES BY ALPHA COUNTING: RUN 2

Solution	Volume (ml)	Plutonium (mg/ml)	Plutonium (mg)
5H-II Feed	710	3.8	2700 (estimated)
5H-I Feed	112	20.89	2340.0
5H-II-1 (Raff.)	205	0.00075	0.15
5H-II-2 (Raff.)	328	0.0103	3.38
5H-II-3 (Raff.)	88	0.0018	0.16
5H-II-4 & W	280	0.0553	15.47

Both feed preparation procedures produced a raffinate with a plutonium concentration well below the one per cent level arbitrarily set for the initial separation step. The hydroxylamine nitrate reduction necessitated a six to sevenfold dilution. The gassing problem encountered with the feed prepared by ferrous sulfamate reduction procedure can probably be eliminated by complete destruction of the sulfamic acid. The lower plutonium separation in Run 2 was attributed to the low acid concentration of the feed solution. Thus, at the present time, both procedures appear to be suitable.

Until now uranium analytical procedures were not available for most of the solutions encountered in this work. Although a number of procedures for uranium determination have been developed, samples which contain more than trace amounts of plutonium-238 have not yet been processed. The uranium-234 in the first solution (B-63) was estimated on the basis of relative mass spectrometric peak heights of uranium-234 and plutonium-238. However, differences in the evaporation rates of the uranium and plutonium from the filament along with the low level of uranium in the sample permitted only an estimation.

Recently, several samples were run by an isotope dilution method. A known amount of a uranium-235-uranium-238 standard was added to the unknown solution. From the relative peak heights of masses 234 and 235, the amount of uranium-234 was calculated. An analysis of the feed solution (5H) indicated about 209 milligrams of uranium-234 as compared to 259 milligrams calculated for the decay of 12.26 grams of plutonium-238 over 32 months. A second analysis indicated that a part of the plutonium elutriate from the first batch of feed solution (B-63-IIC) contained 8.4 milligrams of uranium-234. While results are much better than any previous results, the time laps between sampling and analysis is unsatisfactory. An in-line method of analysis is being sought to reduce the time factor and to increase the accuracy.

The relatively large amount of uranium found in only part of the plutonium elutriate of B63 (eight milligrams compared to 14 milligrams of purified uranium-234) suggests that further work is needed to determine the behavior of uranium in the anion exchange process. Another ion exchange run (5H-III) was made using the hydroxylamine nitrate reducing agent. Samples of the feed solution, raffinate, and wash solution are being analyzed for uranium content. The plutonium elutriate was too dilute for accurate analysis, but this value can be determined by difference. A similar run using the ferrous sulfamate reducing agent will be made, and the two methods will be compared when all the analyses are complete.

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 Separation and Purification

Analysis of Tritium in Helium-3 The absolute accuracy of the gas analysis of tritium in helium-3 by internal geiger counting was checked with a 53.84 atom per cent tritium standard as determined by the mass spectrometer. The sample was diluted 1.160×10^8 times with 98 per cent helium and two per cent isobutane to give a sample of 6.245×10^{-7} atom per cent tritium. Three samples of approximately 0.1 cubic centimeter at atmospheric pressure and 24°C were analyzed. The small sample size gave a count rate of about 4,000 counts per minute so that no errors were introduced with a resolving time correction. The average concentration of three samples was 6.374×10^{-7} atom per cent.

The absolute accuracy of the method is within the precision of 1.25 per cent for the overall method. The standard is now being used to calibrate the new tubes and calculate their resolving times.

Superfluidity The phenomenon of superfluidity in helium-4 below the lambda temperature is presently being investigated. Since helium-3 does not exhibit superfluidity, attempts are being made to use this principle to separate the helium isotopes in the liquid state.

The superfluid system was operated using indium-sealed millipore filters described previously [MLM-1152]. A mixture containing approximately 2.5 per cent helium-3 and 97.5 per cent helium-4 was used as feed. The feed was cooled to below the lambda point by pumping on the surrounding helium bath. After one hour of filtering the flow was stopped and the system was warmed up. The product sample indicated that almost all of the helium-3 was pulled through the filter with the helium-4. The exhaust system contained the helium-3 that was lost.

Carbon Isotope Separation

Thermal Diffusion The objectives of the carbon-13 program are the preparation of 90 per cent pure 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 being used for the removal of heavy gaseous impurities in purified methane, such as nitrogen, carbon monoxide, and ethane. Analyses have shown that the feed methane was not of chemically pure quality (99 per cent minimum). Quality feed material is being obtained.

A five-column system is being revised to use the first three columns for enrichment of methane, the fourth column for carbon rod experiments, and the fifth column for definitive separation experiments.

A four-stage cascade unit of six hot-wire columns was started up using natural methane as feed. The unit is tied to the three concentric-tube unit and is expected to enrich natural methane to about 90 per cent carbon-13.

A two-column thermal diffusion system was used to separate approximately 2.5 liters of methane with a carbon-13 content of 90 to 92 per cent of total carbon. Twelve liters of partially enriched methane were used as feed. The carbon-13 content of the feed gas was approximately 60 per cent of the total carbon. Two 24-foot concentric-tube columns were used. The columns were 1-1/4 inches inside diameter with a concentric 3/4-inch diameter tubular heater. The heater temperature was maintained at 400°C and the cold wall temperature was 15°C. Column pressure was maintained at 750 millimeters of mercury absolute. The columns were initially charged with six liters of feed gas. After a four-day incubation period, gas was removed from the top and bottom of the system twice daily. After each removal, column pressure was restored to 750 millimeters from a feed cylinder. The daily withdrawals ranged from 200 to 400 cubic centimeters at each end. A typical set of mass spectrometric analyses is shown in Table 23.

Table 23

ANALYSIS OF FEED MATERIAL AND PRODUCT OF METHANE PURIFICATION

	Feed (%)	Top Product (%)	Bottom Product (%)
Total Methane	98.38	95.21	93.24
Carbon-13 in Total Carbon	60.86	22.41	91.46

Methane Purification Three additional runs were made on the methane purification system. The first run, No. 26 was designed to duplicate the original runs. The results were inferior to those previously obtained using the same procedures; apparently, system deterioration has occurred. A partial saturation of adsorbents had occurred and necessitated more adequate bake-out procedures or replacement of the adsorbents.

The second of the runs, No. 27, used the large process trap with a small charge for purposes of comparison with the small process trap and similar charge volumes. The analysis for this run was somewhat better than that for Run 26. Analytical uncertainties exist, but the results suggest that some runs should be made with the second trap using low charge volume and fresh adsorbents.

The third of the runs, No. 28, used the large process trap and a withdrawal of two-thirds of the original charge as raffinate, rather than the usual one-third. The analytical results of Run 28 are not complete. Table 24 shows the results of Runs 26 and 27.

Table 24

METHANE PURIFICATION

Experiment Number	Composition (%)				Product Quantity (liters)
	Feed		Product		
	Methane	Carbon-13	Methane	Carbon-13	
26	99.0	1.04	99.7	1.04	12.7
27	99.0	1.04	99.9	1.05	9.6

Thermal Decomposition Studies Two additional runs were made in the thermal decomposition studies using carbon-sheathed Nichrome V wire. The wire, approximately 12 inches long, was constructed by slipping carbon tubes, one to two inches in length, over a 1/16-inch diameter Nichrome V wire. Each carbon tube had approximately a 0.125-inch outer diameter and a 0.070-inch inner diameter. The ends of the tubes were bevelled so they would interlock. Table 25 shows the data obtained to date.

Table 25

**THERMAL DECOMPOSITION OF CARBON MONOXIDE USING A
CARBON-SHEATHED NICHROME V WIRE**

Sheath Temperature (°C)	Pressure (mm Hg)	Decomposition of Carbon Monoxide (%)	
		Pressure Data	Mass Spectrograph Data
810	656.1	3.06	0.91
850	661.1	3.00	1.26
900	711.5	2.99	1.23
925	689.9	1.53	1.36
955	588.3	1.26	1.18
1005	687.3	0.93	1.04
1080	618.3	1.24	0.47

Wire Heating by Alternating Current The wire used in the AC heating studies was a 15-foot length of coiled Nichrome V wire (1/16-inch diameter) which was straightened and stretched about four inches using a turnbuckle device. The wire was cut to 12 feet and suspended between chucks. The wire length between the chucks was 143-7/16 inches. The wire expanded linearly when heated then shrunk slightly as it came to equilibrium at a particular temperature. As the electrical current to the wire was increased, the wire vibrated in a complex wave form in all planes perpendicular to the wire. Just before the wire became incandescent at about 25 amperes, the vibrations suddenly stopped. At this point no visible motion existed; however, faint vibrations could be felt when a block of wood was held against the wire. There was no visible motion when the current was increased to 30 amperes heating the wire to 840°C. Vibrations occurred again when the wire was slowly cooled below a red heat.

If the wire was heated rapidly (29 seconds) to 840°C, no vibrations occurred. With rapid cooling of the wire from 840°C to below red heat in seven seconds, no vibrations occurred. Further experiments will be performed to determine the effect of weight, length, and magnetic fields as functions of the vibrations.

Chemical Exchange and the Prediction of Equilibrium Constants Urey and Greiff¹ were among the first to recognize the differences in chemical properties of isotopic substances for predicting equilibrium constants from molecular data. Their calculations, however, were superseded in a later article by Urey² in 1947, in which the earlier calculations were revised. In the later article the ratios of partition functions for six systems involving carbon-13 were given, including C¹³O₂⁻, C¹³O₂, C¹³, HC¹³N, C¹³O, and C¹³N⁻. Combinations of these

¹ H. C. Urey and L. J. Greiff, *J. Am. Chem. Soc.*, 57, 321 (1935).

² H. C. Urey, *J. Chem. Soc.*, 562 (1947).

ratios yield equilibrium constants which predict the extent to which the exchange will take place for the given reaction.

Recently, Melander¹ developed the equations for calculating the equilibrium constants for a number of types of exchange reactions. The development is complete, and there was a discussion of the approximations made and when they become applicable. Urey also discussed the mathematical background for the systems he calculated.²

In using mathematical calculations to determine whether or not a certain reaction will result in enrichment of carbon-13, only simple molecules were considered. Most of these calculations have been checked by experiment. As the molecules become more complex, the approximations become less valid. Hence, the confidence in any such calculation depends on the care in making approximations, and also on the spectral data available for the molecules concerned.

Four different methods were considered for enrichment of carbon-13. The bicarbonate method, one of the most common methods studied, has the advantages of being cheap and simple, but it has the disadvantage of a slow rate of reaction. Reid and Urey³ sought to increase the rate of reaction by heterogeneous catalysis. They varied pressures on the columns from one to 50 atmospheres and calculated the specifications for a system that would produce four grams of carbon-13 at 33 per cent enrichment per day. The system included six columns in cascade, ranging from 78 feet in height to 91 feet.

The use of monoethanolamine and carbon dioxide was studied by Shaposhnikov.⁴ The reaction was catalyzed by carbonic anhydrase. He claimed a 1.32 separation factor in a six-meter column, 15-millimeters in diameter, in 20 hours. The reaction was run between 15° and 25°C. A two-meter column and an aluminum silicate catalyst were used by Semioklin⁵ to obtain a separation of 1.046 in eight hours for the reaction of potassium bicarbonate and carbon dioxide. Taylor found single-stage separation factors of 1.008 and 1.004 at 35°C and 25°C, respectively, for the reaction of monoethanolamine and carbon dioxide.⁶

Another promising method for carbon-13 enrichment is:

This reaction, as reported by Hutchinson, Stewart, and Urey⁷, is rapid; the single stage separation factor was given as 1.026 at 25°C. The disadvantages of the method, besides toxicity, are the polymerization of hydrogen cyanide and a higher cost than the bicarbonate method. The amount obtained by the authors was given as 0.150 gram of 23 per cent carbon-13 per day.

¹ L. Melander, *Isotope Effects on Rates*, Ronald Press, New York, 1960.

² Urey, *loc. cit.*

³ A. Reid and H. C. Urey, *J. Chem. Phys.*, **11**, 403 (1943).

⁴ Y. K. Shaposhnikov, JPRS-2528 (1960).

⁵ I. A. Semioklin, G. M. Panchenkov, and Y. A. Zkurov, CEA-TR-1495 (1960).

⁶ T. I. Taylor, *Annual Progress Report*, TID-16834, 1962.

⁷ C. A. Hutchinson, D. W. Stewart, and H. C. Urey, *J. Chem. Phys.*, **8**, 532 (1940).

The carbon dioxide-carbon monoxide system is desirable because of its single-stage separation factor of 1.086. The difficulty has been in overcoming the slow rate of reaction. Panchenkov et al.¹ used counter-current flow of the gases generated by a hot wire to achieve the exchange; they obtained a separation factor of 1.20 in a 1.65-meter column using 15 millimeters of steam pressure to catalyze the reaction. Temperatures ranged from 725° to 900°C, and the equilibrium time was 24 hours. Chasalov² also used the carbon monoxide-carbon dioxide system and attempted to combine the exchange with thermal diffusion; he showed that some of the separation was due to the exchange.

The nickel carbonyl-carbon monoxide exchange was studied by Spindel.³ The calculated single-stage separation factor of 1.033 at -10°C agreed with the observed value of 1.030 at -10°C.

Thermal Diffusion Theory

A new theory of the operation of the thermal diffusion column was recently developed. The concentration, velocity and temperature gradients in a thermal diffusion column are specified by three differential equations:

$$\nabla \cdot (\eta \nabla) v = \nabla p - \rho \vec{g} \quad (\text{equation of motion})$$

$$\vec{Q} = \lambda \nabla T \quad (\text{equation of energy balance})$$

$$\nabla \cdot \vec{J} = 0 \quad (\text{equation of continuity})$$

where η is the viscosity, λ is the thermal conductivity, ρ is the density, p is the pressure, v is the vertical convective velocity, g is the acceleration due to gravity, T is the temperature, Q is the heat flow, and J is the mass flux. In writing the equations of change in the above form, the assumptions were made that the column is in a quasi-stationary state, and the convective velocity is in the vertical direction only. Jones and Furry solved the above equations with the additional assumptions that the transport coefficients are independent of concentration and that the variation of the concentration in the radial direction is independent of z . Since the Jones and Furry theory is usually in poor agreement with experimental results, the above equations are being solved numerically without these assumptions.

The $\Omega^{(1,1)*}(T)$ collision integrals were calculated for the helium potential function from 100° to 2000°K, at 100-degree intervals. In conjunction with the collision integral calculations and theory being developed here, a generalized potential function for the other inert gases will be developed. As a first approach to this problem, all existing potential functions for the gases which will lend themselves readily to the generalized form utilized in the collision integral theory will be investigated. Approximately 15 potential functions for neon, argon, krypton and xenon were computed and plotted for comparison; the best of these functions will be selected for use in the Ω integral program.

¹ G. M. Panchenkov, I. A. Semioklin, A. G. Maurina, and N. P. Yesshova, JPRS-2455 (1960).

² I. G. Chasolov, Doctoral Dissertation, Columbia University, 1957.

³ W. Spindel, NYO 8771, *Annual Progress Report*, 1962.

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.

Beryllium Analysis by Gamma Activation

A nondestructive analysis of total beryllium in beryllium powder by gamma activation is being investigated. This method of analysis utilizes the low, 1.69-Mev, threshold energy of beryllium for the (γ, n) reaction. The next lowest threshold energy for this reaction is about 2.23-Mev, thus making the analysis completely selective for beryllium.

In the method developed, a 0.5-inch diameter vial containing the beryllium powder was placed on top of 2.5 centimeters of paraffin (neutron moderator), and an antimony-124 source was placed on top of the beryllium sample. A one-inch disk of indium foil was used as a neutron detector. The powder, paraffin, and detector were housed inside a Lucite cylinder (Figure 7) to insure exact reproduction of positioning of the component. Then the cylinder was placed in a 30-gallon drum of paraffin to increase the neutron flux.

If the geometry and the weight of the indium detector remain constant, the neutron flux is dependent only on the weight of beryllium present and the decay of the 60-day half-life antimony-124 source; thus a decay correction is made.

Figure 7. Irradiation Chamber for Gamma Activation of Beryllium

For analysis the gamma source was placed directly over the vial of beryllium and left in that position for exactly one hour. At the end of the irradiation period, the gamma source and the indium detector were removed, and the beta emission of the indium was counted at five-minute intervals for an hour. A decay curve was plotted for indium ($T_{1/2} = 54$ minutes), and the count rate was extrapolated to T_0 (Figure 8), the time at the end of irradiation. The neutron flux was approximately 1×10^4 neutrons per square centimeter per second per gram beryllium, giving a count rate of about 3500 counts per minute per gram indium.

Figure 8. Decay of Indium Detector

A standard curve was made using spectrographic grade beryllium with weights ranging from 0.40 to 1.76 grams. The curve was plotted on an expanded scale graph paper so that the weight of beryllium could be accurately read to one milligram. The plot gave a straight line in the region investigated and showed no variation with particle size (powdered region) or impurities present.

Duplicate analyses were made on two samples from Brush Beryllium and one spectrographic standard; the results were compared with those obtained from the oxide gravimetric determination (Table 26).

This method of analysis required two to three hours, compared to two to three days for the oxide gravimetric method. The precision was better than ± 0.2 per cent.

Table 26

TOTAL BERYLLIUM BY GAMMA ACTIVATION

Beryllium Sample	Beryllium by Gamma Activation ^a (% of sample)	Deviation (%)	Oxide Gravimetric Beryllium (% of sample)
Spectrographic Standard	99.16	± 0.13	99.18
Brush Beryllium Co. No. 7280	99.08	± 0.08	98.97
Brush Beryllium Co. No. 7317	99.09	± 0.04	98.66

^aAverage of two samples.