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SUMMARY

ISOTOPE SEPARATION The Jones and Furry thermal diffusion column theory was used to estimate relative values of separation per unit length for xenon-131 and xenon-136. The calculations show that separation rates can be increased by operating the thermal diffusion column at high pressures using small distances between the hot and cold wall.

A thermal diffusion cascade system, consisting of six hot-wire and three concentric-tube columns, was designed to enrich carbon-13 from 60 to 90 per cent using methane as a feed gas. Experimental measurements on a similar cascade indicate that the impurities would be less than 15 per cent if the feed is 99.5 per cent methane.

RADIOELEMENTS It has been shown that, in the "known" half-life method for determining the resolution time of a counting system, two significant sources of error are unrecognized: (1) a small absolute error in the "known" half-life can produce a relatively large error in the value computed for the resolution time; and (2) the use of unweighted counting data, which has the effect of over-weighting the relatively unreliable lower end of the decay curve, produces inaccurate and imprecise results.

The radioisotopes in a waste stream from the polonium process were identified as iron-59, cobalt-60, selenium-75, silver-110m and antimony-124. Zinc-65, one of the principal impurities, could be removed by hydroxide precipitation.

Differential thermal analysis data were taken on potassium plutonium sulfate, plutonium sulfate and potassium sulfate. An expression for the solubility product control was derived and is being checked at this time.

Calculations were completed for the shielding required to protect personnel from gamma radiation from a one-kilogram source of plutonium-238. Thicknesses of lead, iron, uranium, and concrete that would be required to reduce the total gamma radiation to one milliroentgen per hour at one meter were found to be 0.065, 1.47, 0.19, and 9.78 centimeters respectively.

ANALYTICAL

Calorimetry The half life of thorium-227, calculated using a double variation of the growth curve of actinium-227, was calculated to be 18.729 ± 0.048 days. This corresponds to a measured half life of 21.772 ± 0.004 years for actinium-227, and to 11.434 ± 0.005 days for the half life of radium-223.

Mass Spectrometry An electron multiplier was installed in the cycloid tube of a CEC Model 21-620-A mass spectrometer. The high gain of the multiplier (approximately 10^5) will aid in the detection of trace impurities and will increase instrument sensitivity by a factor of 100. The counting of individual ions will also be possible because of the inherently fast response time of the multiplier.

Reduction of Heavy Metal Cations Heavy metal ions were reduced with sodium borohydride at pH 3.0. Of these metals bismuth, copper, nickel, palladium and antimony precipitated quantitatively at a pH of 2. The pH of the solution increased to nine during the course of the precipitation.

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.

XENON ISOTOPE SEPARATION AND PURIFICATION

Thermal Diffusion: The temperature-corrected Jones and Furry thermal diffusion column theory was used to estimate relative values of separation per unit length for xenon-131 from xenon-136. The parameter H^2/K where H is the usual thermal diffusion transport coefficient and K is the total thermal diffusion mixing coefficient, which is proportional to separative work per unit length, was calculated for wire and heater sizes from 1/16 to 1/2 inch for hot wall temperatures from 606° to 1192°C, and for cold wall diameters from 3/8 to one inch at 20°C. The results are given in Tables 1 and 2 for hot-wall temperatures of 606° and 899°C. All calculations were based on operation at a pressure for which $K_c = 10K_D$ (90 per cent of maximum separative work).

Table 1

THERMAL DIFFUSION COLUMN CHARACTERISTICS FOR $Xe^{131} - Xe^{136}$, HEATER TEMPERATURE OF 606°C

Hot Wall Diameter (in)	Cold Wall Diameter (in)	Operating Pressure (torr)	$H^2/K \times 10^6$
0.5	0.75	945	18.6
	0.6875	1481	24.6
	0.625	2784	36.4
0.33	0.750	403	7.82
	0.6875	525	9.23
	0.625	715	11.04
	0.5	1730	18.5
0.25	0.75	298	5.99
		286	4.71
	0.625	465	6.04
	0.5	890	9.65
	0.375	2672	18.8
0.125	0.75	209	3.34
	0.5	455	4.26
	0.375	803	4.89
0.063	0.75	167	1.91

For a given temperature, the calculations show that separation rates can be increased by operating at high pressures and small gaps. For instance, a 1/4-inch heater in a 3/8-inch column gives (at 900°C) a value of 45.7×10^{-6} for H^2/K and a 1/4-inch heater in a 1/2-inch column gives 23.8×10^{-6} . Operating pressures for these two columns are 3591 and 1177 torr respectively. Comparable figures for a 1/16-inch wire in a 3/4-inch column are 5.9×10^{-6} for H^2/K and 214 torr for the operating pressure.

Table 2
THERMAL DIFFUSION COLUMN CHARACTERISTICS FOR
Xe¹³¹ - Xe¹³⁶, HEATER TEMPERATURE OF 899°C

Hot Wall Diameter (in)	Cold Wall Diameter (in)	Operating Pressure (torr)	H ² /K x 10 ⁴
0.5	0.1	425	26.3
	0.75	1265	44.4
	0.6875	2000	58.2
	0.625	3776	88.5
0.33	0.750	532	19.96
	0.6875	695	23.0
	0.625	950	27.2
	0.5	2327	45.5
0.25	0.75	379	13.12
	0.75*	362	13.47
	0.625	624	17.0
	0.5	1177	24.31
	0.375	3591	45.7
0.125	0.75*	269	9.75
	0.5*	595	12.8
	0.375*	1024	13.5
0.063	0.75*	214	5.93

* Calculated from Hot-Wire Shape Factors

If a separation factor of 125 is required for the xenon system and if a production rate of five liters per day is specified, then a good estimate of the size of the thermal diffusion column system can be obtained from ideal cascade calculations. Results of such calculations are given in Table 3.

Table 3
SYSTEM CHARACTERISTICS FOR XENON ISOTOPE SEPARATION

Heater and Column Size	System Length (feet)	Total Column Length (feet)
1/16-inch wire in 3/4-inch tube	170	3182
1/4-inch heater in 3/8-inch tube	26	413
1/4-inch heater in 1/2-inch tube	53	777

THEORETICAL RESEARCH

Cascade Theory A cascade of six hot wire and three concentric tube columns (see Figure 1) was designed to enrich carbon-13 from 60 to 90 per cent using methane as a process gas. The column dimensions and separation parameters are summarized in Table 4. The cascade will have an equilibrium time of 20 to 40 days and will produce 0.04 grams per day of enriched methane. Experimental measurements on a similar cascade indicate impurities should be held to less than 15 per cent if the feed is 99.5 per cent methane.

Table 4

DIMENSIONS, OPERATING CONDITIONS, AND SEPARATION PARAMETERS

	Hot Wire	Concentric Tube
r_1 (cm)	0.9525	1.5875
r_2 (cm)	0.07937	0.9525
T_1 (°C)	20	20
T_2 (°C)	650	400
L_{eff} (cm)	700	700
P (torr)	760	760
H (g/sec)	2.73×10^{-5}	2.49×10^{-5}
K (g/sec cm)	1.57×10^{-2}	4.67×10^{-3}
$\epsilon = H/\frac{1}{2}K$	0.813×10^{-3}	2.66×10^{-3}
$\delta \nu$ (g/sec cm)	1.11×10^{-3}	3.31×10^{-3}
$\delta \nu$ (g/day cm)	9.6×10^{-4}	2.86×10^{-3}
η - viscosity index used to calculate H & K	0.8	1

Cascade theory is usually developed for a cascade containing one type of columns. For the above cascade, which contains two types of column, it was necessary to generalize the theory in the following manner. Since the separation properties of a column, namely the transport coefficients H and K , appear in the cascade equations only through the two generalized parameters

$$Y = \frac{HL}{2K}$$

and

$$\phi = \frac{P}{\nu H}$$

one is lead to consider introducing the following quantities:

ν_E = the number of hot-wire columns to which a concentric tube column is equivalent.

L_E = the length of hot-wire column to which a concentric tube column is equivalent.

P = product flow.

Figure 1

CASCADE OF 6 HOT WIRE COLUMNS AND 3 CONCENTRIC TUBE COLUMNS
(Feed gas is methane containing $\frac{1}{2}\%$ impurities)

Using the above equations one finds that

$$L_E = \frac{H_c}{H_w} \frac{K_w}{K_c} L_c$$

$$\nu_E = \frac{H_c}{H_w} ,$$

where the subscripts w and c refer to hot wire and concentric tube columns, respectively. The cascade calculations are performed for the above cascade by considering it to be composed of two sizes of hot wire columns. The generalization of this method to any number of different columns is apparent, viz. for the i 'th type

$$L_{Ei} = \frac{H_i}{H_j} \frac{K_i}{K_j} L_i$$

$$\nu_{Ei} = \frac{H_i}{H_j}$$

where the j 'th type of column is the reference.

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.

DETERMINATION OF COINCIDENCE CORRECTION

The resolution time (resolving time, dead time, insensitive time) of a counting system is that period of time after the recording of an event during which the system is incapable of recording another event. For counting purposes, the event which renders the system insensitive and those events which follow within the resolution time, τ , are in coincidence. The difference between the number of events which occur and those which are recorded is the coincidence correction, and, at high counting rates, this correction can represent a significant percentage of the true number of events occurring.

One of the methods for quantifying the resolution time of a counting system, that of following the decay of a nuclide of accurately known half-life, has been repeatedly rediscovered and refined. Most recently, Martin¹ has pointed out that the method, as usually applied, lacks precision, since it involves the extrapolation of the statistically inaccurate "tail" of the decay curve in order to evaluate the losses at higher counting rates.

To correct this source of error, Martin rearranges the basic equation for coincidence correction to permit the use of the statistically more reliable counting rates at the upper end of the decay curve.

Martin's refinement, while a distinct improvement over previously reported applications of the "known half-life" method, leaves uncorrected two basic sources of error which are generally unrecognized. The most important of these arises from the fact that a small absolute error in the "known" half-life can produce a relatively large error in the computed value of τ . Conversely, an error in the value of τ used originally in determining the "known" half-life can produce an absolute error in that half-life which is not reflected by the statistically computed probable error.

A second source of error arises from the use of unweighted counting data, a practice which has the effect of giving excessive weight to the unreliable lower end of the decay curve in the determination of a slope either by graphical methods or by least squares computations.

Table 5 illustrates the effect of an error in the "known" half-life on the value of the resolution time as computed by the method of least squares. The alpha counting rate of lead-211, a decay product of actinium-227, was determined at two-minute intervals over a period of more than four hours. (Although lead-211 is a beta-emitter, its decay product, bismuth-211, is an alpha-emitter with a 2.15 minute half-life, and it is convenient to follow the decay of lead-211 by alpha-counting after the bismuth-211 achieves radioactive equilibrium).

¹Martin, G. R., Nuclear Instruments and Methods, 13, 263 (1961)

Table 5

COMPUTED RESOLUTION TIME AS A FUNCTION OF ASSUMED HALF-LIFE

(Data for Lead-211; $T_{1/2} = 36.1 \pm 0.2$ min.)

Assumed $T_{1/2}$ (min.)	Computed r (min. $\times 10^3$)		Rejects ^b
	(unweighted data)	(weighted data) ^a	
35.90	1.823 $\pm$ 0.177	1.310 $\pm$ 0.004	1
35.92	1.762 0.176	1.301 0.004	1
35.94	1.701 0.175	1.292 0.004	1
35.96	1.640 0.174	1.283 0.004	1
35.98	1.580 0.174	1.275 0.004	1
36.00	1.519 0.173	1.266 0.004	1
36.02	1.458 0.173	1.257 0.004	1
36.04	1.397 0.172	1.248 0.004	1
36.06	1.336 0.172	1.228 0.004	3
36.08	1.275 0.172	1.218 0.004	3
36.10	1.214 0.172	1.209 0.004	3
36.12	1.152 0.172	1.192 0.004	4
36.14	1.091 0.172	1.183 0.004	4
36.16	1.030 0.172	1.173 0.005	4
36.18	0.969 0.173	1.163 0.005	4
36.20	0.908 0.173	1.153 0.005	4
36.22	0.847 0.174	1.143 0.005	4
36.24	0.786 0.174	1.150 0.006	2
36.26	0.725 0.175	1.141 0.006	2
36.28	0.663 $\pm$ 0.176	1.131 $\pm$ 0.006	2
36.30	0.602 $\pm$ 0.177	1.122 $\pm$ 0.006	2

^aChauvenet's criterion used to reject inconsistent data^bNumber of points rejected by Chauvenet's criterion out of a total of 82.

Since the half-life of lead-211 is reported to be 36.1 ± 0.2 minutes² the value of r was computed for 21 half-life values ranging from 35.9 to 36.3 minutes. Column 2 of Table 5 shows the results obtained when the data were not weighted; Column 3 shows the results for weighted data to which Chauvenet's criterion for the rejection of inconsistent points was applied.

In Table 6, the converse case is shown, to illustrate the effect of an error in r on the computed value of the half-life. Column 2 gives the results for unweighted data; Column 3 gives those for weighted data with Chauvenet's criterion applied.

²Sargent, B. W., Can. J. Research, **17A**, 103 (1939)

Table 6

COMPUTED HALF-LIFE AS A FUNCTION OF ASSUMED RESOLUTION TIME (T)

(Data for Lead-211; $T_{1/2} = 36.1 \pm 0.2$ min.)

Assumed τ (min. x 10 ⁷)	Computed Half-Life (minutes)				Rejects ^b
	Unweighted Data		Weighted Data ^a		
0.750	36.513	± 0.021	36.582	± 0.020	13
0.800	36.468	0.019	36.524	0.018	13
0.850	36.422	0.017	36.465	0.016	13
0.900	36.376	0.016	36.405	0.014	13
0.950	36.331	0.014	36.347	0.012	13
1.000	36.285	0.012	36.287	0.010	13
1.050	36.238	0.010	36.265	0.010	9
1.100	36.192	0.009	36.197	0.008	9
1.150	36.146	0.007	36.151	0.008	6
1.200	36.099	0.007	36.080	0.007	5
1.250	36.052	0.007	36.011	0.007	3
1.300	36.005	0.007	35.933	0.007	1
1.350	35.958	0.009	35.848	0.009	0
1.400	35.911	0.010	35.755	0.011	0
1.450	35.864	0.012	35.661	0.014	0
1.500	35.816	0.014	35.568	0.017	0
1.550	35.768	0.016	35.475	0.020	0
1.600	35.720	0.018	35.382	0.023	0
1.650	35.672	0.020	35.289	0.026	0
1.700	35.624	0.022	35.197	0.030	0
1.750	35.575	0.024	35.105	0.033	0

^aChauvenet's criterion used to reject inconsistent data^bNumber of points rejected by Chauvenet's criterion out of a total of 82.

It is clear from Table 5 that relatively minute errors in the supposedly known half-life can produce substantial differences in the computed value of the resolution time. It is also apparent that the computed probable error of the resolution time, which is merely a measure of the statistical precision and consistency of the data, does not reflect the absolute accuracy of the determination.

Table 6 shows that, if the "known" half-life was originally determined with a counting instrument subject to resolution losses, the absolute accuracy of the counter resolution time is of far greater importance to the absolute accuracy of the half-life determination than would be suggested by the reported probable error.

Thus, the computed values of the half-life and the resolution time are interdependent and must be treated as such in the determination of either by counting methods.

A method, adapted from the variational method proposed by K. C. Jordan¹ for the least squares treatment of calorimetric data, has been adapted for the determination in a proportional counter of half-life and resolution time as two unknown interdependent quantities. The method is basically the one indicated by Tables 5 and 6; viz., various arbitrary values are assigned to either the resolution time or the half-life, and the other quantity is calculated by the method of least squares. From the principle of least squares, it is assumed that the most reliable answer is the one which gives the smallest sum of the squares of the deviations.

A plot of the data in either Table 5 or Table 6 would yield a parabola, with the assumed value as abscissa and the computed probable error as ordinate. A computer program has been written which, by an iterative technique, determines the coordinates of the vertex of the parabola with either the half-life or the resolution time treated as "known". The results of applying this program to the lead-211 data used for Tables 5 and 6 are not yet available, but will be reported next month.

WASTE DISPOSAL RESEARCH

A sample of "caustic" waste solution was analyzed by radiochemical techniques. Caustic waste originates in the polonium purification process: all fumes and vapors generated in the polonium concentration and purification operations are scrubbed through a tank of concentrated sodium hydroxide. In addition, any overflow from the various dissolution and denitrification steps is fed to the same tank. Predictably, the main nuclide was polonium-210. Other isotopes identified in the solution were: iron-59, cobalt-60, selenium-75, silver-110m, and antimony-124.

An additional step requiring the precipitation of aluminum hydroxide (at pH 7), after the precipitation of bismuth hydroxide (at pH 12), was introduced in the treatment of high-level radioactive wastes in the hydrolysis cells. Gamma-ray pulse height analysis of the supernatant solutions before and after the aluminum hydroxide precipitation showed that this step effectively removed zinc-65, one of the major radioactive species present in waste solutions resulting from the decanning operation.

POTASSIUM PLUTONIUM SULFATE

Plutonium(IV) ions react with potassium sulfate to form an insoluble compound, potassium plutonium sulfate, as shown in Equation (1).

Solubility studies, differential thermal analyses, thermogravimetric analysis and stability studies are being made to investigate the nature of potassium plutonium sulfate.

The solubility product constant K_{sp} is defined by Equation (2).

$$K_{sp} = [K^{+}]^4 [Pu^{+4}] [SO_4^{-2}]^4 \quad (2)$$

However, since sulfate ions form complexes with plutonium(IV), potassium and hydrogen ions, the K_{sp} function is somewhat more complicated than indicated by Equation (2). An expression, shown in Equation (3), has been developed to describe the solubility of potassium plutonium sulfate in acid solutions.

$$[K^{+}]^4 \gamma^4 [Pu^{+4}]^* = K_{sp} \left[\frac{1}{[SO_4^{*}]^4 \beta^4} + \frac{K_1}{[SO_4^{*}]^3 \beta^3} + \frac{K_1 K_2}{[SO_4^{*}]^2 \beta^2} + \frac{K_1 K_2 K_3}{[SO_4^{*}] \beta} + K_1 K_2 K_3 K_4 \right] \quad (3)$$

¹Jordan, K. C., Manuscript in preparation

where

K_{sp} = solubility product constant of $K_4 Pu(SO_4)_4 \cdot 2H_2O$

K_1, K_2, K_3, K_4 = formation constants of $PuSO_4^{++}$, $Pu(SO_4)_2^+$, $Pu(SO_4)_3^-$, and $Pu(SO_4)_4^{--}$, respectively.

$[K^*]$ = total potassium concentration which is equal to $[K^+] + [K SO_4^-]$

$[Pu^*]$ = total plutonium concentration which is equal to $[Pu^{+4}] + [PuSO_4^+] + [Pu(SO_4)_2^+] + [Pu(SO_4)_3^-] + [Pu(SO_4)_4^{--}]$

$[SO_4^*]$ = total sulfate concentration which is equal to $[H SO_4^-] + [SO_4^{--}]$

β = fraction of dissociated sulfate which is equal to $\frac{[SO_4^{--}]}{[SO_4^*]}$

γ = fraction of dissociated potassium which is equal to $\frac{[K^+]}{[K^*]}$

A conditional solubility product constant K_{sp}^* may be defined as

$$K_{sp}^* = [K^*]^4 \gamma^4 [Pu^*] \quad (4)$$

Another term Ψ may be defined as

$$\Psi = \frac{1}{[SO_4^*]^4 \beta^4} + \frac{K_1}{[SO_4^*]^3 \beta^3} + \frac{K_1 K_2}{[SO_4^*]^2 \beta^2} + \frac{K_1 K_2 K_3}{[SO_4^*] \beta} \quad (5)$$

Combining Equations (3), (4) and (5) yields:

$$K_{sp}^* = K_{sp} \Psi + K_{sp} K_1 K_2 K_3 K_4 \quad (6)$$

The formation constants K_1 , K_2 , and K_3 are listed in Table 7. The K_{sp} and K_4 can be determined by measuring the solubility of $K_4 Pu(SO_4)_4 \cdot 2H_2O$ in solutions of varying sulfate concentration. When K_{sp}^* is plotted against Ψ , the slope of the straight line is equal to K_{sp} and the intercept is equal to $K_{sp} K_1 K_2 K_3 K_4$.

The solubility of $K_4 Pu(SO_4)_4 \cdot 2H_2O$ in two molar acid solutions of lithium sulphate at 25°C are shown in Figure 2. The plot of K_{sp}^* as a function of Ψ , shown in Figure 3, indicates that K_{sp} is $10^{-17.3}$ and K_4 is $10^{-0.5}$. These results are not final since only one study has been completed. Solubility as a function of acidity, and solubility as a function of potassium concentration must be determined before reliable values can be assigned to K_{sp} and K_4 .

Table 7

FORMATION CONSTANTS FOR PLUTONIUM-SULFATE COMPLEXES

	Complex	$-\Delta F$ (K cal.) 2.33 M (H ⁺) ^a	Log K_f^* 2.33 M (H ⁺)	Log K_f
K_1	$Pu(SO_4)^{++}$	3.91	2.83	4.33
K_2	$Pu(SO_4)_2^+$	2.93	2.11	3.61
K_3	$Pu(SO_4)_3^-$	0.95	0.69	2.19
K_4	$Pu(SO_4)_4^{--}$	?	?	?

^aSeaborg and Katz, The Actinide Elements, McGraw-Hill Book Company, Inc., (1954) p. 347.

Figure 2

SOLUBILITY OF $K_2Pu(SO_4)_6 \cdot 2H_2O$ IN ACID SULFATE SOLUTION AT 25°C
(2M Acid Solutions)

Figure 3

CONDITIONAL SOLUBILITY PRODUCT CONSTANT AS A FUNCTION OF ψ

Samples of $K_4Pu(SO_4)_4 \cdot 2 H_2O$ and $Pu(SO_4)_2 \cdot 4 H_2O$ were prepared for thermogravimetric analysis and differential thermal analysis. Results of wet chemical analysis of both compounds are shown below:

Compound	% Plutonium (theoretical)	% Plutonium (found)	% $SO_4 =$ (theoretical)	% $SO_4 =$ (found)
$Pu(SO_4)_2 \cdot 4 H_2O$	47.50	47.28	38.18	38.28
$K_4Pu(SO_4)_4 \cdot 2 H_2O$	29.30	29.27	47.11	47.22

The incomplete results of the thermogravimetric analysis and differential thermal analysis of the two compounds are shown in Figures 4 and 5. The thermogravimetric curve for $Pu(SO_4)_2 \cdot 4 H_2O$ compares favorably with a similar analysis made at New Brunswick Laboratory (NBL-165, page 20).

The first significant weight loss by $Pu(SO_4)_2 \cdot 4 H_2O$ and by $K_4Pu(SO_4)_4 \cdot 2 H_2O$ (Figure 4) corresponds to the loss of water from both compounds. The second break corresponds to the loss of two SO_3 molecules by each compound. Thus, the residue at the completion of ignition of $Pu(SO_4)_2 \cdot 4 H_2O$ should be PuO_2 , and the residue upon ignition of $K_4Pu(SO_4)_4 \cdot 2 H_2O$ to $800^\circ C$ should be $K_4PuO_2(SO_4)_2$, or more likely $2 K_2SO_4 + PuO_2$.

Figure 4

WEIGHT LOSS OF SULFATE COMPOUNDS AS A FUNCTION OF TEMPERATURE

Figure 5

DTA OF SULFATE COMPOUNDS

Stability of $K_4Pu(SO_4)_4 \cdot 2H_2O$ On September 10, 1962, $K_4Pu(SO_4)_4 \cdot 2H_2O$ was prepared from plutonium nitrate solution. The plutonium was 81.13 per cent plutonium-238. The compound was placed in a closed container and has been analyzed by weight and calorimetric procedures. The stability of the compound over a six-month period is shown below:

Date Analyzed	Weight (g)	Pu^{238} (g) ^a	Total Pu (g)	% Pu Found	% Pu Theory
9-14-62	2.8875	0.6853	0.8467	29.25	29.23
12- 4-62	2.7721	0.6571	0.8099	29.22	29.23
2- 6-63	2.6237	0.6179	0.7616	29.23	29.23

^aDecayed back to September 14, 1962

PLUTONIUM-238 GAMMA SHIELDING

The shielding required to protect personnel from exposure for eight hours to the gamma radiation from one kilogram of plutonium-238 were calculated. The calculations were made using lead, iron, uranium and concrete, and were based upon a specific activity of 6.43×10^{11} disintegrations per second per gram for the three principal gamma components, 43 kev (0.038 per cent), 99 kev (0.009 per cent), and 150 kev (0.001 per cent) where the percentage values are absolute intensities, i.e. unconverted photons per 100 disintegrations.⁴

⁴Steindler, M. J., (1962) Radiation Problems Associated with the Handling of the Actinide Series, ANL-6540.

The bare source dose rate in air was calculated from

$$R = \sum_i R_i = \sum_i \frac{I_i}{4\pi r^2} \frac{\mu_{ai}}{\rho} \frac{1}{K}$$

where

R_i = The dose rate of the i-th component in roentgens per hour at a given distance.

r = The given distance.

I_i = The gamma ray intensity of the i-th component in disintegrations per second per unit mass.

μ_{ai} = The linear absorption coefficient of air for each component in inverse centimeters.

ρ = The density of air (g/cc).

K = The conversion constant to roentgens.

The bare source dose rates are tabulated below:

Component (Mev)	Dose Rate (mr/hr)
0.043	12.8
0.099	48.6
0.150	0.7

The linear attenuation coefficients were calculated (by extrapolation, where necessary) from the mass absorption coefficients³ and are given below:

Component (Mev)	Lead	Iron	Uranium	Concrete
0.043	95.2	22.9	211.3	1.14
0.099	60.0	2.65	19.8	0.397
0.150	20.9	1.41	45.3	0.327

The attenuations required to reduce the exposures to less than 1.0 milliroentgens per hour correspond to the values of the dose rates. Using these attenuations, the required thickness for each material was calculated using the following equation:

$$\frac{I_o}{I} = \text{attenuation} = e^{\mu_o x}$$

where I is the transmitted intensity, I_o is the incident intensity, μ_o is the linear attenuation coefficient in inverse centimeters, and x is the thickness of the material in centimeters. The attenuating thickness by

³Gradstein, G. W., X-Ray Attenuation Coefficients from 10 kev to 100 Mev, NBS Circular 583 (April 30, 1957)

component is given below:

Component (Mev)	<u>Attenuating Thickness in cm</u>				Dose Rate (mr/hr)
	Lead	Iron	Uranium	Concrete	
0.043	0.027	0.11	0.012	2.23	1.0
0.099	0.065	1.47	0.19	9.78	1.0
0.150	0.0	0.0	0.0	0.0	0.7

Although gamma rays of 0.203, 0.760 and 0.875 Mev are present to less than 0.001 per cent of the total activity, their contribution to the shielding was computed, but found to be negligible. The total dose rate at the thickness required to reduce the maximum gamma contributor to 1.0 milliroentgens per hour was then computed, and is shown below:

	Lead	Iron	Uranium	Concrete
Thicknesses (cm)	0.165	1.47	0.19	9.78
Dose Rate (mr/hr)	1.22	1.09	1.0	1.0

The following assumptions are implicit in these calculations:

1. A point source and isotropic radiation.
2. No self-absorption in the source.
3. Compton scattering not included.
4. Linear interpolation was used for some of the coefficients, although their variation is non-linear.
5. A unity build-up factor.

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.

CALORIMETRY

The Half-Life of Thorium-227 from the Power Growth of Actinium-227, by the Double Variational Method

A variational method of applying least squares to curve fitting for representing half-life data was described previously (MLM 1148). The variational method was demonstrated by solving for the half-life of thorium-227 using a double variation of the growth curve of actinium-227 (Sample Z-18) as measured with Calorimeter 51. The final result gives a half life of 18.729 ± 0.048 days, and corresponds to 21.772 ± 0.004 years for the half life of actinium-227 and 11.434 ± 0.005 days for the half life of radium-223. The errors are absolute probable errors, i.e., the limits are expected to have a 50 per cent chance of encompassing the true half-lives.

Chemical separation of the actinium-227 in Sample Z-18 took place on December 15, 1952. The first measurement was made on December 17, 1952 at 4:10 p.m. Zero time in this report is taken as 12 Noon on the latter date.

Neglecting the shorter half-lives of 21 minutes for francium-223, 36.1 minutes for lead-211, etc., the power growth curve of actinium-227 can be represented by Equation (1).

$$W(t) = W_1 e^{-\lambda_1 t} - W_2 e^{-\lambda_2 t} + W_3 e^{-\lambda_3 t} \text{ (watts)} \quad (1)$$

where the subscripts 1, 2, and 3 refer to actinium-227, thorium-227, and radium-223, respectively. The constants W_1 , W_2 , and W_3 are related to each other. However, in order for these relationships to be valid an exact zero time of separation, branching ratio of actinium-227 to thorium-227 and francium-223, etc., must be known. Therefore these constants were solved from the calorimeter data.

The solution for W_1 and λ_1 was begun 551 days from $t = 0$ when contribution from the other two terms were negligible. The result was $W_1 = 0.073168$ watts and $\lambda_1 = 0.0000871658 \text{ days}^{-1}$ which corresponds to a half life for actinium-227 of 21.772 years (MLM-1140). Subtracting each $W(t)$ from $W_1 \exp(-\lambda_1 t)$ reduces Equation 1 to Equation 2.

$$P(t) = W_2 e^{-\lambda_2 t} - W_3 e^{-\lambda_3 t} \quad (2)$$

Equation 2 will be solved by the double variational method. Experimental data and calculated $P(t)$ for Equation 2 is given in Table 8.

The double variational solution of Equation 2 has been programmed for the IBM-1620 on Program 26. Input data in this case will be columns 1 and 3 of Table 8 and six λ 's, three representing λ_2 and three for λ_3 . The half-lives corresponding to the six λ 's, that were chosen are given in columns 2 and 3 of Table 9. Program 26 first computes the most probable values for W_2 and W_3 for each pair of half-lives and the corresponding sum of the deviations squared (columns 4 and 5 of Table II). The normal equations for these computations are:

$$\sum P e^{-\lambda_2 t} = W_2 \sum e^{-2\lambda_2 t} + W_3 \sum e^{-(\lambda_2 + \lambda_3)t} \quad (3)$$

$$\sum P e^{-\lambda_3 t} = W_2 \sum e^{-(\lambda_2 + \lambda_3)t} + W_3 \sum e^{-2\lambda_3 t} \quad (4)$$

Table 8

CALORIMETRIC DATA ON Z-18 AND CALCULATED P(t) FOR EQUATION 2

(1) t (days)	(2) W(t) (watts)	(3) P(t) (watts)
0.174	0.0015464	0.0716214
1.990	0.0028301	0.0703249
5.171	0.0057385	0.0673974
13.063	0.0148041	0.0582808
85.063	0.0663807	0.062470
97.983	0.0685936	0.039518
114.005	0.0701845	0.022598
118.000	0.0704833	0.019358
131.988	0.0711322	0.011986
135.000	0.0712321	0.010797
139.006	0.0714051	0.008815
140.988	0.0714402	0.008338
152.993	0.0716279	0.005705
160.005	0.0717556	0.003988
166.094	0.0717790	0.003377
182.000	0.0718495	0.0016666
187.975	0.0718413	0.0013727
204.944	0.0718050	0.0006705
224.944	0.0716964	0.0005037

The sum of the deviations squared in each case is calculated by Equation 5 (column 6, Table 9).

$$\sum d_i^2 = \sum (P(t) - W_2 e^{-\lambda_2 t} + W_3 e^{-\lambda_3 t})^2 \quad (5)$$

For each set in Table 9 Program 26 calculates a parabola that passes through the three $\sum d_i^2$ as a function of the corresponding half-life of thorium-227. For example, the parabola for Set 1 is:

$$(T_{1/2} - 18.714284)^2 = 1.24635 \times 10^{-4} (\sum d_i^2 - 7399.29048) \quad (6)$$

and the three constants are listed in rows 2, 3, and 4, column 1, Table 10. Equation (6) can be interpreted as follows: 18.714284 is the most probable half-life of thorium-227 if the true half-life of radium is equal to 11.458304 days, and if the extrapolation was not carried too far or if the system is not too nonlinear. An equivalent statement applies to the F of the parabola (1.24635×10^{-4}) and the minimum sum of the deviations squared (7399.291). The probable error of a single observation (P.E.S.O.) and the probable error of thorium-227,

derived from Equation 6, also have the same meaning. Thus, according to Equation (3) in MLM-1149 -

$$P.E.S.O. = 0.6745 \sqrt{\frac{\sum d_i^2}{n-q}} = 0.6745 \sqrt{\frac{7399.29}{19-3}} = 14.505 \text{ microwatts} \quad (7)$$

Table 9

**LEAST SQUARES SOLUTION OF $P(t) = W_2 e^{-\lambda_2 t} - W_3 e^{-\lambda_3 t}$
USING ASSUMED VALUES FOR λ_2 AND λ_3**

(1) Set Number	(2) Assumed Half-Life of Radium-223 (days)	(3) Assumed Half-Life of Thorium-227 (days)	(4) W_2 (watts)	(5) W_3 (watts)	(6) Sum of Deviations Squared d_i^2 (micro-watt) ²
1	11.458304	18.7064063	0.158303175	0.086557430	7449.125
	11.458304	18.7251041	0.157983777	0.086234619	7493.116
	11.458304	18.7438393	0.157665197	0.85912611	8097.943
2	11.439960	Same as	0.158015207	0.086272273	7547.668
	11.439960	Set No. 1	0.157697581	0.085951238	7254.933
	11.439960		0.157380765	0.08563099	7522.759
3	11.4216748	Same as	0.157729442	0.085989304	7853.833
	11.4216748	Set No. 1	0.157413569	0.085670029	7225.466
	11.4216748		0.157098498	0.083515388	7157.381

Table 10

**EXTRAPOLATED OR INTERPOLATED QUANTITIES DERIVED FROM
TABLE II VERSUS ASSUMED HALF-LIFE VALUES OF RADIUM-223**

	Set 1	Set 2	Set 3
(1) Assumed Half-Life of Radium-223 (days)	11.458304	11.439960	11.4216748
(2) Most Probable Half-Life of Thorium-227 (days)	18.7142840	18.725520	18.736744
(3) Minimum Sum of Deviations Squared (microwatt) ²	7399.291	7254.795	7117.252
(4) F of parabola (days ² - microwatts ⁻²)	1.24635 $\times 10^{-6}$	1.249957 $\times 10^{-6}$	1.2535810 $\times 10^{-6}$
(5) Probable Error of a Single Observation (microwatt)	14.505	14.363	14.226
(6) Probable Error in $T_{1/2}$ Th ²²⁷ (days)	0.016193	0.016058	0.015928
(7) Most Probable Value of W_2 (watts)	0.15816861	0.15769052	0.15721693
(8) Most Probable Value of W_3 (watts)	0.08642142	0.08594410	0.08547127

Since there are 19 observations and we are solving for only three unknowns at the present time (W_2 , W_3 , and λ_2), the probable error in the half-life of thorium-227 is

$$P.E. T_{1/2} (Th^{227}) = \sqrt{F} (P.E.S.O.) = 0.01619 \text{ days} \quad (8)$$

These results are listed rows 5 and 6 of Table 10. The most probable values of W_1 and W_2 are listed in rows 7 and 8. They were obtained by assuming straight line relationships of W as a function of $T_{1/2}(Th^{227})$ of Table 9 and the most probable value of $T_{1/2}$ of Table 10.

From Table 10 the assumed half life of radium-223 can be plotted as a function of the corresponding most probable half-life of thorium-227. Assuming a straight line, the equation relating the two half lives is given as:

$$T_{1/2}(Th^{227}) = 25.73268 - 0.6125164 T_{1/2}(Ra^{223}) \quad (9)$$

In a previous report (MLM-1135) the half-life of radium-226 was reported as 11.434 days. Substituting this value in Equation (9), the most probable value for the half life of thorium-227 is 18.729 days. The probable error in this value can be calculated easily if we know the probable error in the radium-223 half life. From MLM-1135 and more recent analyses of the data it is believed that the absolute probable error is 11.434 ± 0.005 days. By Equation (9), the reflection of this probable error in the half life of thorium-227 is $0.6125 \times 0.005 = 0.0031$ days. The probable error in the half life of thorium-227, assuming no error in the half-life of radium-223, is 0.0160 days (by Table 10). It seems reasonable to expect that the absolute probable error is about three times greater or 0.048 days.

Combining the two probable errors, since they are mutually exclusive, gives

$$P.E. (Th^{227}) = \sqrt{(0.048)^2 + (0.003)^2} = 0.0481 \text{ days} \quad (10)$$

At this point, the answer for this particular problem was obtained; however, Program 26 does not stop but continues and finds the most probable value for all four constants. A major parabola is fitted to rows 2 and 3 of Table 10 in the same manner that the minor parabolas were fitted to columns 3 and 4 of Table 9. The result is:

$$(T_{1/2} - 18.96728)^2 = 40.017 \times 10^{-6} (\sum d_i^2 - 5756.3) \quad (11)$$

where 18.96728 is the most probable value for the half life of thorium-227 for any half-life value of radium-223, of course qualified by the degree of extrapolation and linearity of the system. The probable error is calculated as before, except that $q = 4$ instead of 3, and is 0.0836 days. This is 5.2 times greater than when solving for three constants, i.e. with the radium-223 half life fixed at 11.434 days. Program 26 now calculates the most probable value for radium-223 by grouping the half-life combinations in Table 9 such that the abscissa of the minor and major parabolas is the half-life of radium-223. The final result is 11.07936 ± 0.12070 days.

By a sense switch Program 26 can reiterate the entire procedure. The half-lives just calculated can be set in the input, and spread each value either one or 0.1 probable errors. In this problem 0.1 probable errors was chosen, so the next pass used the following six half-lives: 18.948976, 18.942576, 18.9361808, 11.081557, 11.0726067, and 11.0636710. The second pass and the third pass were almost identical, indicating convergence. The final result was as follows:

$$T_{1/2}(Th^{227}) = 18.93957 \pm 0.07254 \text{ days} \quad (12)$$

$$T_{1/2}(Ra^{223}) = 11.08413 \pm 0.1259 \text{ days} \quad (13)$$

$$\sum d_i^2 (\text{min.}) = 5832.9 (\text{micro-watt})^2 \quad (14)$$

Notice that the half-life of radium-223 is 0.35 days less than the much better value of 11.434 ± 0.005 days. The difference is only 2.8 probable errors, and it is our experience that internal consistency probable errors such as given in Equation (11) are likely to be low by a factor of three. Therefore, it can be considered that this system was nearly statistical, and consequently increases our confidence that the half-life of thorium-227 is 18.729 ± 0.048 days.

MASS SPECTROMETRY

To reduce sample processing time and increase instrument sensitivity a magnetically focused electron multiplier was installed in the cycloid tube of a CEC Model 21-620-A mass spectrometer. The design of the multiplier is similar to those built by White, et. al.⁴ Certain modifications were necessary because of the small amount of available space in the cycloid tube.

The ion beam in the cycloid tube is separated by crossed electric and magnetic fields, causing the ion beam to travel in a cycloid as shown in Figure 6 (a). The magnetic field is provided by a permanent magnet of approximately 1500 gauss. The electric field is generated by a series of six plates held at successively lower potentials. Five of the six plates are similar to the one shown at the bottom in Figure 7. The remaining plate termed the "zero" plate appears at the bottom in Figure 8.

The zero plate also serves as a mounting base for the other five plates, the collectors, and the source. The instrument as originally designed covers two mass ranges on two different collectors. The high mass range covers approximately masses 12 through 150 and uses the cycloidal focusing principle. The low mass range is used for masses less than 12 and utilizes a Dempster type instrument by removing the electric field. Since the magnetic field strength could be reduced to 1500 gauss, mass 2 ions can be collected on the high mass, cycloidal focusing collector. Thus, the low mass range system is extraneous, and the electron multiplier was put into the space originally occupied by it.

The electron multiplier also uses crossed electric and magnetic fields to focus the secondary electrons generated at each stage of the multiplier. Thus, all stages of the multiplier can be a single sheet of semiconducting material. The semiconductor must release several electrons when it is struck by a charged particle. It must also have a high resistivity so that the electric field can be maintained by applying a potential across the multiplier slab. A second slab of the same material is used so that the electric field will have a component perpendicular to the surface of the multiplier plate. The positioning of the two slabs is indicated in Figure 6 (b) which also shows the magnetic and electric fields and the path of the electrons.

A major modification to White's multiplier was required because of the location of the multiplier with respect to the incident ion beam. If the beam had been allowed to strike the upper semiconductor slab, the secondary electrons would have traveled to the right in Figure 6 (a). Since the length of each slab had to be about two centimeters long to achieve the necessary gain, they would interfere with the primary ion beam in this case. A separate first dynode was added to "reflect" the beam to the bottom slab for multiplication (see Figure 6 (b)).

The material used for the initial trial of the multiplier was n-type gold-doped silicon with a room temperature volume resistivity of 10^5 ohm-centimeter (as used by White). Since the resistivity required for operation was higher by approximately 100 times, the material had to be cooled with chilled helium in the tube, shown in Figure 8 on the upper zero plate.

The multiplier slabs were insulated from each other and from the zero plate by aluminum oxide slabs as shown in Figure 6 (b). This also illustrates the method of clamping the multiplier assembly in place on the zero plate. Figure 9 shows the multiplier assembled on the zero plate and the lead wires from each end of the silicon slabs to the base connector.

⁴F. A. White, J. C. Sheffield, and W. D. Dairs, "Semiconductors Yield Improved Electron Multiplier", Nucleonics, 19, 8, 58-60, (Aug., 1961)

Figure 6 (a)

ION PATHS IN STANDARD CYCLOID TUBE

Figure 6 (b)

ELECTRON MULTIPLIER

Figure 7
MULTIPLIER SLABS

Figure 8
ZERO PLATES

Figure 9

MULTIPLIER ASSEMBLED ON BASE PLATE

Results The cycloid tube containing the multiplier was used successfully without employing the multiplier. In this trial the standard high gain integrating amplifier was used to amplify the ion beam striking the first dynode. This configuration was successful even with the high potentials applied to the multiplier plates.

The initial tests of the multiplier however, were not successful. It is being used as a preamplifier for the same integrating amplifier mentioned above. One peak has been observed, but it is felt that this peak is an anomaly as the height indicates a multiplier gain of only 100 and the accelerating voltage does not correlate with any previously determined accelerating voltages. Since the first dynode in conjunction with the multiplier must operate at a very high negative potential, it may be disturbing the primary ion beam.

REDUCTION OF HEAVY METAL CATIONS

The use of sodium borohydride as an analytical reagent for the precipitation of heavy metal cations from a nitric acid solution at pH 1 has been investigated. Cations of nickel, bismuth, iron, copper, silver, antimony and tellurium have been reduced and precipitated from solution.

The precipitate formed on the reduction of a given cation with sodium borohydride redissolved in the solution at pH 1 or below. Tests were run at pH 3 to determine if the precipitate would remain. Unfortunately, a medium of this acidity could not be maintained under the experimental conditions, so no attempt was made to control the hydrogen ion concentration during the reaction for this set of experiments.

In the typical experiment, 10 milliliters of a 0.2-molar solution of a given cation were placed in a 250-milliliter beaker. The volume was increased to approximately 50 milliliters with distilled water and one-normal sodium hydroxide as required, to adjust the pH to one or two. Thirty milliliters of a one-molar aqueous sodium borohydride solution were added. In this step the pH of the medium was not controlled, as in previous experiments, but was permitted to increase as the reduction progressed. A black precipitate that was rapidly produced was subsequently filtered through a tared crucible and washed with distilled water. The filtrate was tested for completion of the precipitation process by the addition of more sodium borohydride. No further precipitate appeared.

Each precipitate was then dried at 120°C for about 17 hours, weighed, and dissolved in nitric acid. These solutions obtained were subsequently analyzed for metal content. Results of the experiments are shown in Table 11.

The results shown in Table 11 indicate that the reactions were quantitative. The relatively high weight values obtained for the precipitate as compared with the theoretically expected amounts can be attributed to oxide or boride formation, and the presence of other possible contaminants in the precipitate.

Table 11

REDUCTION OF METALLIC CATIONS WITH SODIUM BOROHYDRIDE

Precipitate	Total Precipitate (g)	Theoretical Metallic Content of Precipitate (g)	Metallic Content Determined Analytically (g)	pH Change
Bi	0.4505	0.418	0.4160	2-8.8
Cu	0.1507	0.1271	0.1140	2-9.3
Cu	0.0763	0.1271	0.1263	2-9.8
Ni	0.1812	0.1174	0.1141	2-8.9
Ni	0.1726	0.1174	0.1141	2-9.5
Pd	0.2176	0.2128	0.2096	1.5-8.5
Pd	0.2928	0.2128	0.1168	1-9.2
Sb	0.1435	0.1218	-	1.5-9
Fe	-	-	-	-

Notes:

The relatively high weights obtained for the precipitates as compared to the calculated theoretical weights can be attributed to oxide, or boride formation and other possible contaminations of the precipitate.

The fine black precipitate obtained in the case of iron obstructed filtration.