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QUANTITATIVE RADIOCHEMICAL METHODS FOR THE DETERMINATION OF THE SOURCES OF NATURAL RADIOACTIVITY, PART II*

By

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By John N. Rosholt, Jr.

ABSTRACT

The study of the state of equilibrium of any natural radioactive source requires the analysis for several key nuclides or groups of nuclides to determine their contribution to the total amount of radioactivity. The methods used for the radiochemical analysis of Th^{232}, Th^{230}, Pa^{231}, and Ra^{226} ~~are~~ are described. Alpha activity measured by scintillation counting is used for the determination of these nuclides.

Standardization independent of ore standard comparison is proved necessary for the determination of Rn^{222} and Pb^{210} and the methods for determining these independently are shown. Independent and comparative values for the other nuclides are used to prove that the method of independent standardization is valid.

INTRODUCTION

The usefulness of the determination of the component sources of natural radioactivity has been shown and the radiochemical methods of analysis for Rn^{222}, Pb^{210}, and Th^{232} described (Rosholt, 1954). A more complete analysis of the state of equilibrium will include some additional long-lived radionuclides and groups of equilibrium-established short-lived daughters, namely: Th^{230}, Ra^{226}, and the Pa^{231} group in the U^{235} series. Thus the state of equilibrium can be rigorously defined if the contents of the following components are known: (1) uranium group, (2) Th^{230}, (3) Ra^{226}, (4) Rn^{222} group,

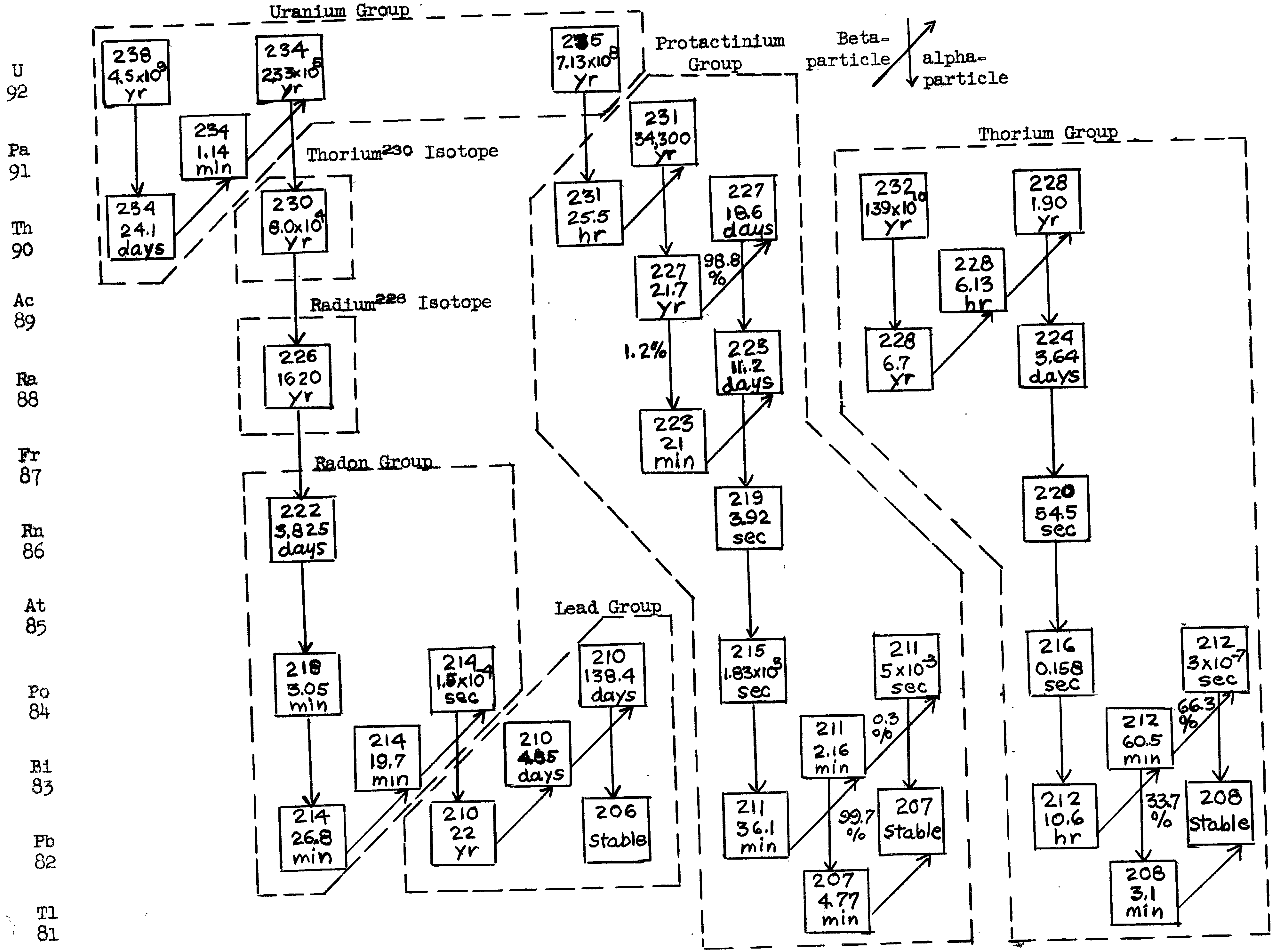

Figure 1.--Classification of natural radioactivity in separate groups.

(5) Pb^{210} group, (6) Pa^{231} group, and (7) Th^{232} series. The relations of these components are shown in figure 1. Components 1 through 5 describe what can be termed the state of equilibrium. The Th^{232} series, though not involved in the description of equilibrium, is a major contributor of radioactivity which must be determined. Where a more rigorous definition is desired, the contribution of the state of equilibrium of the U^{235} series defined by the Pa^{231} content must be considered.

Throughout this paper equivalent units are used. Uranium and thorium content is given as actual percent of uranium or thorium. All of the disintegration products in the three decay series are expressed as equivalents to the parent nuclides.

When equilibrium exists in a decay series, the disintegration rate of each product is identical to that of the parent. Thus the amount of pure daughter product expressed in percent equivalent will equal the amount of pure parent nuclide expressed in percent which would be required to establish equilibrium between the daughter and parent. The decay rate of this theoretically required amount of pure parent will equal the decay rate of the amount of pure daughter present.

In the case of the U^{235} series, the parent U^{235} is expressed equivalent to U^{238} by use of the abundance and half-life ratios. Any product in the U^{235} series will be expressed in percent equivalent to U^{238} plus U^{235} which would theoretically be required for equilibrium and the activity of the U^{235} decay series product would be 4.5 percent of the equivalent U^{238} value. For example 100 mg of 1 percent uranium of normal isotope abundance in equilibrium with all of its decay products would contain the following amounts and activities of decay products:

An aluminum ring, 50-mm diameter by 3-mm high with 0.005-gauge cellophane glued to its under side, is used for the ZnS-precipitate mount. Plastic cement is spread on the periphery of the under side of the ring directly on the cellophane, and the precipitate and membrane are mounted by adherence to this surface. A 47-mm ring without the cellophane protector is used to mount the bismuth sulfide-carried precipitate.

Reagents and sources

1. 0.014 molar Bi_2O_3 in 5 percent HCl solution (6 mg Bi/ml).
2. 0.014 molar $Pb(NO_3)_2$ solution (3 mg Pb/ml).
3. 0.090 molar $FeCl_3 \cdot 6H_2O$ solution (5 mg Fe/ml).
4. 0.110 molar $ZrCl_4$ solution (10 mg Zr/ml).
5. 0.1 molar $Na_4P_2O_7$ solution.
6. 0.146 molar $BaCl_2 \cdot 2H_2O$ solution (20 mg Ba/ml).
7. $Pr(NO_3)_3 \cdot 6H_2O$ salt.
8. Oxalic acid, crystals.
9. Zinc sulfide, powder, phosphorescent grade, nonactivated.
10. 0.03 millicurie Pb^{210}, Bi^{210}, Po^{210} source solution.
11. 0.05 millicurie Ra^{226} source solution.
12. Pa^{231} source, naturally occurring 18 percent equivalent Pa^{231}, 10 percent equivalent Th^{230} sample (Th^{230}, Pa^{231}, Ac^{227}, Th^{227} source).
13. NBS 1.0×10^{-9} gm Ra^{226} standard solution.
14. Standard pitchblende ore, MSOR, 44.96 percent uranium.
15. NBS standard 2230-1, MS-VL, 3.08 percent uranium.
16. NBS standard 2230-2, MS-L, 6.92 percent uranium.
17. NBS standard, 1.0 percent uranium,
18. $Th(NO_3)_4 \cdot 4H_2O$ reagent (10 year old Th^{228} source).
19. $Th(NO_3)_4 \cdot 4H_2O$ equilibrium reagent (48 years old).
20. NBS standard, 1.0 percent thorium.

Procedure for separation of nuclides

The sample, 1 gram or less depending on total activity and ease of solution, is fused to almost red heat with 4 to 5 grams of Na_2O_2 in a nickel crucible. The melt is taken up in water, neutralized with concentrated HCl, and made up to an acidity of 1.0 normal with HCl and a total volume of 100 ml. With this treatment the sample should be completely in solution. Six milligrams of bismuth carrier is added, and the solution, at about 45° C, is gassed with H_2S.

The bismuth and polonium isotopes used for the Rn^{222} and Pb^{210} determination are separated from the solution when the bismuth sulfide carrier is precipitated and filtered from the solution (Rosholt, 1954). The Rn^{222} isotope was removed temporarily when the sample was fused.

The filtrate containing the uranium, protactinium, thorium, actinium, radium and lead isotopes is made almost free of H_2S by evaporation on a hot plate to a volume of approximately 80 ml. Ten drops of 1+1 H_2SO_4, 10 mg of zirconium carrier, 3 ml of $Na_4P_2O_7$ are added separately to the filtrate and the solution is boiled gently for 1 to 2 minutes while the $(ZrO)_2P_2O_7 \cdot ThP_2O_7$ precipitate is forming (Carney and Campbell, 1914). The hot solution containing the precipitate is immediately centrifuged, the supernatant liquid poured off, and the time recorded. The precipitate is washed with distilled H_2O, centrifuged, and wash supernatant combined with the centrifugate. The precipitate is retained for either the Th^{230} determination or the Th^{232} determination where Ra^{224} is allowed to build up. This method for Th^{232} is used where the activity of Bi^{212}-Po^{212} is too low for accurate measurement as previously described (Rosholt, 1954).

1 milliliter of $Na_4P_2O_7$ reagent are added to the gently boiling centrifugate, and the solution centrifuged and washed again. The centrifugate is adjusted to a pH of 3 with NH_4OH, cooled and gassed with H_2S for 5 minutes while 150 mg of ZnS is added. An excess of sulfide ion is required to adsorb completely the Pb^{212} contained in the solution on the ZnS; Bi^{212} and Po^{212} are also adsorbed. The zinc sulfide is filtered from the solution and the time recorded. Twenty milligrams of barium carrier is added and 3 drops of 1+1 H_2SO_4 added precipitating $BaSO_4 \cdot RaSO_4$. The precipitate is allowed to settle. An additional 150 mg of zinc sulfide phosphor is added, the slurry mixed, filtered, washed, mounted, and dried.

Measurement of Th^{230} and Pa^{231}

The praseodymium oxalate carrier precipitate will contain the Th^{230} along with the Pa^{231}, Ac^{227}, and Th^{227} alpha emitters when products of the U^{235} decay series are present and the Th^{232} and Th^{228} alpha emitters if any Th^{232} decay series is present. Some Bi^{211} alpha activity may be present depending on the amount of U^{235} series decay products in the sample and the time elapsed since the thorium separation because Pb^{211}-Bi^{211} decaying with a 36.1-minute half-life is carried along with the thorium isotopes.

The counting rate of the precipitate is measured at day-to-day intervals for 6 to 10 days. Long counting measurement periods are used for determining these rates in order to establish the amount of Ra^{223} growth from Th^{227} for the Pa^{231} determination. The Th^{230} nuclide and Pa^{231} group are resolved by use of a plot of a straight-line equation of the form:

$$C_T = C_{Pa^{231}} f_{Th^{227}} + C_{Th^{230}}$$

where C_T is the measured counting rate

$C_{Pa^{231}}$ is the Pa^{231} counting rate

$C_{Th^{230}}$ is the Th^{230} counting rate

$f_{Th^{227}}$ is the function of the growth of Ra^{223} and disintegration products from Th^{227}.

The time at which the $Pr_2(C_2O_4)_3 \cdot 10H_2O$ precipitate was filtered is used as the zero time from which the function of Th^{227} is calculated. The function of Th^{227} with time is shown in figure 2 and is plotted from the data obtained from calculation 4. The plot of the straight-line equation is shown in figure 3. The intercept of the Th^{230}-Pa^{231} line at the zero axis is the counting rate of Th^{230} and the slope of the line is the Pa^{231} counting rate.

The Th^{230} and Pa^{231} analysis by this method is limited to samples which do not contain quantities of the Th^{232} decay series in excess of 1/50 for the ratio of percent Th^{232}/percent equivalent Pa^{231}. Quantities of Th^{232} series in excess of this amount can usually be detected in the Bi_2S_3 precipitate used for the Rn^{222} analysis. The lower analytical limit for Th^{230} and Pa^{231} is approximately 0.01 percent equivalent.

Efficiency calculation and standardization of the Th^{230}, Pa^{231}, and Ra^{223} measurements.--Th^{230}, Pa^{231}, Ac^{227}, and Th^{227} are separated from 4 grams of a natural occurring source sample which contains 18 percent equivalent Pa^{231} and immediate disintegration products, 10 percent equivalent Th^{230}, 13 percent equivalent Ra^{226}, and 0.1 percent uranium. The sample of high-grade Pa^{231} source is digested with 20 ml of HCl for half an hour, filtered, and the soluble portion retained. Bismuth and polonium isotopes are removed from the solution, and the Th^{230}, Pa^{231}, Ac^{227}, and Th^{227} separated by coprecipitation with $(ZrO)_2P_2O_7$ carrier. The pyrophosphate precipitate is dissolved in oxalic acid, and the solution is adjusted to a pH of 3 with NH_4OH. Two

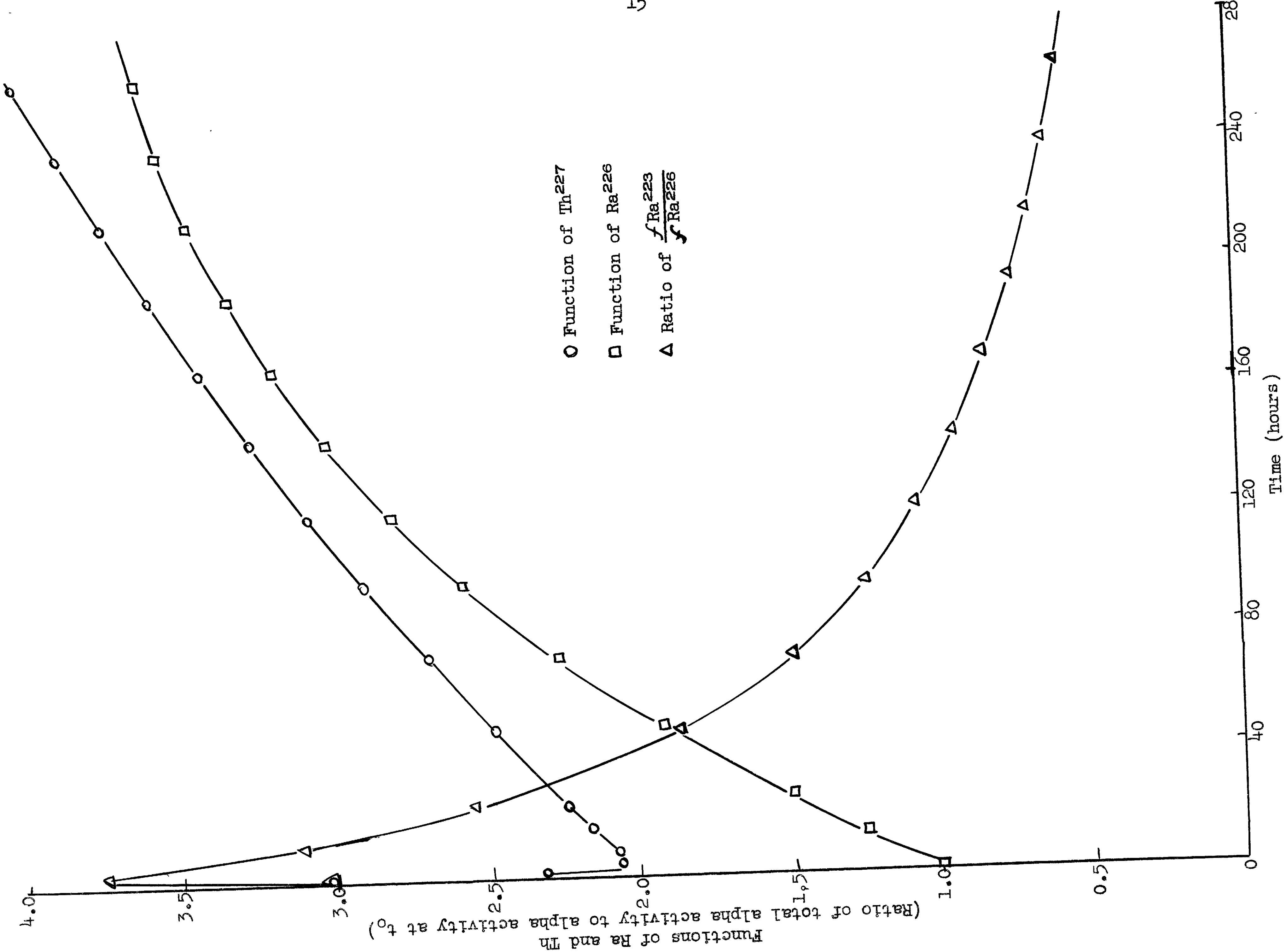

Figure 2.--Decay curves for straight-line equations.

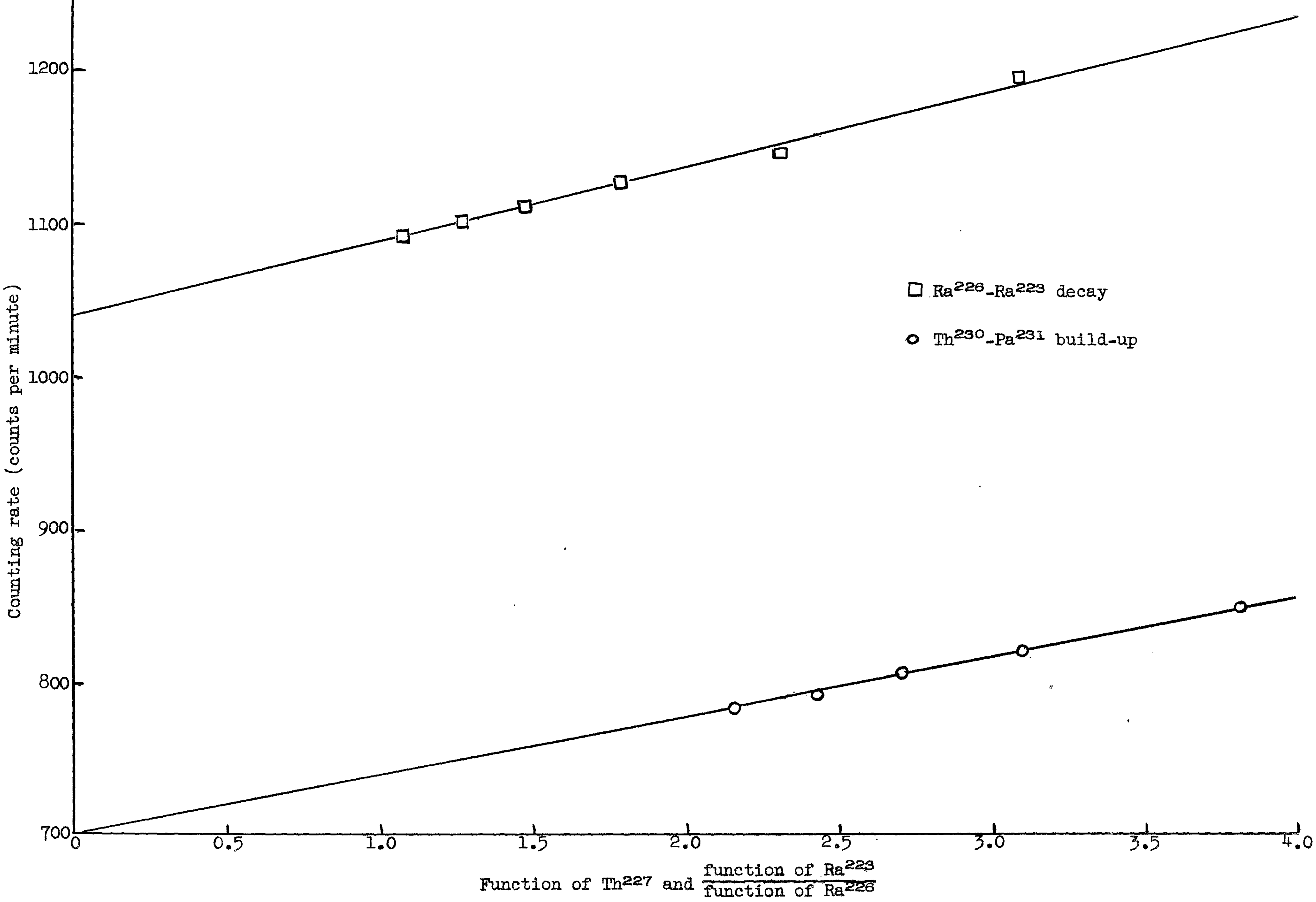

Figure 3.--Plot of straight-line equations.

hundred milligrams of zinc sulfide and 10 drops of HF are added, the slurry is stirred for 5 minutes, filtered, washed, and dried, and the time recorded.

Small fractions of this active zinc sulfide are used for the source of the Th^{230} and Pa^{231}-Ac^{227}-Th^{227}. Each individual source which should represent 300-1000 alpha-particle disintegrations per minute is thinly spread on the center of a 50-mm aluminum ring-supported paper and placed in the automatic sample changing scintillation detector. The alpha particle counting rate is measured at approximately once a day for 10 to 15 days. The straight-line equation for Th^{230} and Pa^{231} is calculated and plotted using the data from these measurements. The counting rates of the Th^{230}, Pa^{231}-Ac^{227}-Th^{227}, and Ra^{223} are determined from this plot. These counting rates are then calibrated to total alpha particle disintegration rates using the appropriate factor of detection efficiency for the phototube used from table 1.

The active zinc sulfide source is transferred to a nickel crucible and carried through the separation steps for the normal Th^{230}-Pa^{231} and Ra^{226}-Ra^{223} analyses. The counting rates of the Th^{230}, Pa^{231}, and Ra^{223} isotopes are compared to the total alpha particle disintegration rates measured in the zinc sulfide source. The efficiencies of the Th^{230} and Pa^{231} analyses are calculated and the standard counting rates of Th^{230} and Pa^{231} determined (calculation 9). The standard counting rates of Th^{230} and Pa^{231} are also determined from several standard uranium ore samples. Table 2 shows these efficiency values and the comparison of the separately determined standard counting rates.

Greater variation exists between each determination of the efficiency of the measurement of Th^{230}, Pa^{231}, and Ra^{223} than between each determination for the other nuclides because of the difficulty of adsorbing sufficient carrier-free activity of these nuclides.

Table 1.--Values used for calculation of the detection efficiencies of the 3-inch photomultiplier tube.

Phototube used	Ra^{226} activity in ZnS source detected by phototube (c/min)	Ra^{226} content by radon train analysis 1/ (10^{-9} g of Ra^{226})	Ra^{226} activity calculated from Ra^{226} content (dis/min)	Detection efficiency (ratio of measured activity to theoretical activity)	Ratio: Po^{210} activity in phototube normalized to Po^{210} activity in tube 4 (av. 14 ZnS sources)	Normalized ratio x detection efficiency of tube 4
1	3885 ± 36	1.885 ± 0.015	4081 ± 32	0.952 ± 0.012	0.984 ± 0.008	0.955 ± 0.018
3	5040 ± 40	2.397 ± 0.011	5190 ± 24	0.971 ± 0.009	0.998 ± 0.003	0.969 ± 0.016
4	3475 ± 26	1.652 ± 0.024	3577 ± 52	0.971 ± 0.016	1.00	0.971 ± 0.016
5	5239 ± 45	2.607 ± 0.021	5644 ± 45	0.928 ± 0.011	0.955 ± 0.016	0.928 ± 0.022
6	4168 ± 52	2.003 ± 0.020	4336 ± 43	0.961 ± 0.015	0.989 ± 0.005	0.960 ± 0.017

1/ Radium analyses by Sylvia P. Furman, U. S. Geological Survey.

Table 2.--Experimental alpha activity constants for Th^{230} and Pa^{231} determinations.

Sample	Efficiency (percent)		Standard counting rate (c/min/mg equivalent)	
	Th^{230}	Pa^{231}	Th^{230}	Pa^{231}
ZnS source	57.5	57.9	422	19.6
	57.1	60.4	420	20.4
	61.4	63.0	451	21.3
	65.7	60.6	482	20.5
	61.8	63.9	454	21.6
	57.6	57.8	423	19.6
	58.9	56.5	433	19.1
	61.7	63.2	453	21.4
	63.5	61.9	466	20.9
	58.6	59.2	430	20.0
Average and standard deviation	60.4 ± 2.9	60.4 ± 2.4	444 ± 21	20.4 ± 0.8
MS-OR(44.96%U)			467	20.4
MS-L(6.92%U)			480	22.1
MS-VL(3.08%U)			434	20.3
			468	21.7
			447	20.8
			462	22.0
			449	21.0
			468	20.4
NBS(1.0%U)			433	20.3
			470	21.0
Average and standard deviation			458 ± 16	21.0 ± 0.7

Measurement of Ra^{226}, Ra^{223}, and Rn^{222}

The barium sulfate carrier precipitate will contain the Ra^{226} alpha emitter and the Ra^{223}-Rn^{219}-Po^{215}-Bi^{211} alpha emitters in the presence of the U^{235} decay series, and the Ra^{224}-Rn^{220}-Po^{216} alpha emitters when the Th^{232} decay series is present. The analysis of Ra^{226} and Ra^{223} by this method is limited to the same restrictions for the ratio of Ra^{223}/Th^{232} as those imposed for the Th^{230}-Pa^{231} analysis.

The counting rate of the precipitate is measured at approximately equally spaced intervals such that 5 to 7 measurements are made over a period of 2 to 4 days. Long periods of measurement are required in order that the amount of Ra^{223} decaying may be calculated. The Ra^{226} and Ra^{223} components are resolved by use of a plot of a straight-line equation of the form:

$$\text{since } C_T = C_{Ra^{223}} f_{Ra^{223}} + C_{Ra^{226}} f_{Ra^{226}}$$

$$\text{then } C_T/f_{Ra^{226}} = C_{Ra^{223}} (f_{Ra^{223}}/f_{Ra^{226}}) + C_{Ra^{226}}$$

where C_T is the measured counting rate

$C_{Ra^{223}}$ is the Ra^{223} counting rate

$C_{Ra^{226}}$ is the Ra^{226} counting rate

$f_{Ra^{223}}$ is the function of the decay of Ra^{223} and decay products

$f_{Ra^{226}}$ is the function of the growth of Rn^{222} and decay products.

The time of the $BaSO_4$ filtration is used as the zero time from which these functions are calculated. The function of Ra^{226} and the ratio of the function of Ra^{223} to the function of Ra^{226} are shown in figure 2. They are plotted from the data obtained from calculations 5 and 6. The plot of the straight-line equation is shown in figure 3. The intercept of the Ra^{226}-Ra^{223} line at the $f_{Ra^{223}}/f_{Ra^{226}}$ value of zero is the counting rate of Ra^{226} and the slope of the line is the Ra^{223} counting rate.

The Ra^{223} content determined from this precipitate should agree rather closely with the Pa^{231} content found in the Th^{230}-Pa^{231} precipitate. The average of these two values is then used for the Pa^{231} content.

The analysis for Ra^{226} by scintillation method is restricted to samples which do not contain more than 20 mg of barium plus strontium. The same restriction regarding the presence of the Th^{232} decay series products exists for Ra^{226}-Ra^{223} as for Th^{230}-Pa^{231}. In the special case where Ra^{228}, Th^{228}, and Ra^{224} from the Th^{232} decay series and Ra^{226} are present in a sample that contains Th^{228} exceeding 95 percent of the total initial alpha activity in the thorium precipitate, the straight-line equations modified for Ra^{224} presence may be used to calculate the Ra^{226}, Th^{228}, and Ra^{224} content of the sample. In all other limited cases the Ra^{226} analysis is performed by the radon train method. The lower analytical limit for Ra^{226} using the scintillation counter is approximately 0.001 percent equivalent.

The method for the determination of Rn^{222} has been described (Rosholt, 1954).

Efficiency calculation and standardization of Ra^{226}-Ra^{223} measurement and Rn^{222} measurement.--The Ra^{226} and Rn^{222} source is a 10^{-7} curie aliquot of the Ra^{226} solution. A 50-ml volume containing this source is boiled under partial vacuum while flushing with air to remove the radon. Radon decay products are removed from the solution by adsorption on zinc sulfide at a pH of 1 to 3. It was determined that more than 99 percent of the bismuth and polonium activity is adsorbed on zinc sulfide up to an acidity of 0.5 normal HCl. Two drops of 1+1 H_2SO_4 and 150 mg of zinc sulfide are added, and the slurry is filtered, washed, and dried. The time of precipitation is recorded. In the presence of sulfate ion the zinc sulfide will adsorb an appreciable amount of $RaSO_4$ from the solution. Small fractions of this carrier-free active zinc sulfide are made into separate samples of the desired amount of activity and prepared for counting in the same manner as with the Th^{230} source.

The counting rates of the carrier-free sources are measured at regular intervals for a few hours. The amount of pure Ra^{226} activity detected is determined by extrapolation of the increasing counting rate back to the time of filtration. Several of the $RaSO_4$ sources are used to calculate the detection efficiency of the preceding measurements. These sources are dissolved in HCl, and a radium analysis of the solution is performed by the radon train method (Curtiss and Davis, 1943). The value of the Ra^{226} activity determined by the photomultiplier tube measurement is compared to the total Ra^{226} activity calculated from the Ra^{226} content determined by the conventional radium analysis (calculation 8). The ratio of these two values is used as the detection efficiency factor (table 1). A National Bureau of Standards 10^{-9}-g Ra^{226} standard solution is used to calibrate the radon train analysis.

Rn^{222} is allowed to build up for 3 days or more in the active zinc sulfide sources which are to be used for over-all efficiency calculation. The counting rate of the Ra^{226} and Rn^{222} plus Po^{218} and Po^{214} which are almost in equilibrium with the Rn^{222} in the source is determined. For a radon build-up period of 3 to 5 days, the product of 0.334 and the difference between the original activity of Ra^{226} and the latter activity of the Ra^{226}, Rn^{222}, Po^{218} and Po^{214} is the activity of Rn^{222} at the time of the latter measurement (see calculation 11). The activities of both the Ra^{226} and Rn^{222} are corrected to yield total disintegration rates by use of the appropriate detection efficiency factor.

The active zinc sulfide is immediately transferred to a nickel crucible. The daughter products of Rn^{222} are separated and the counting rate of the

Bi_2S_3 precipitate for Rn^{222} analysis is determined in the usual manner. The solution is carried through the separation procedure to the isolation of the radium isotopes. The $(ZrO)_2P_2O_7$ carrier was precipitated and separated even though no thorium isotopes are present in order to simulate the actual conditions of analysis of a sample. The counting rate of Ra^{226} is measured and compared to the total disintegration rate of the Ra^{226}, thus allowing calculations of the efficiency and the standard counting rate of the Ra^{226} analysis (calculation 9).

The Ra^{223}, allowed to build up in the carrier-free Th^{230}-Pa^{231} precipitate, is carried through the radium isotope procedure. The efficiency and standard counting rate of Ra^{223} and its immediate daughters are calculated from this data (calculation 9).

Uraniferous samples will contain both Ra^{226} and Ra^{223} isotopes. The counting rates of Ra^{226} and Ra^{223} plus its immediate daughters in the standard ore samples are compared to the theoretical counting rates of these isotopes calculated from the over-all efficiency values of these determinations and the data is shown in table 3.

The over-all efficiency of the Rn^{222} determination is calculated from the ratio of the counting rate of the Po^{214} in the Bi_2S_3 precipitate and the total disintegration rate of the Rn^{222} computed on the $RaSO_4 \cdot ZnS$ source at the time of fusion. The standard counting rate is calculated from this efficiency value (calculation 10), and the values are shown in table 4.

The determination of the standard counting rate of Rn^{222} using ore samples in which the determination is independent of Rn^{222} loss has been performed. A standard uranium ore in a nickel crucible is placed in a refrigerator freezing compartment at -22° C to impound the radon. After the sample has remained in the freezer for three weeks, attaining approximately 98 percent

Table 3.--Experimental alpha activity constants for Ra^{226} and Ra^{223} determinations.

Sample	Efficiency (percent)		Standard counting rate (c/min/mg equivalent)	
	Ra^{226}	Ra^{223}	Ra^{226}	Ra^{223}
ZnS source	89.2	92.9	655	31.4
	89.0	90.1	654	30.4
	88.8	87.5	652	29.6
	89.1	85.0	655	28.7
	88.1	86.8	647	29.3
	90.1	93.8	662	31.7
	90.4	85.3	664	28.8
	90.0	89.8	661	30.4
	89.1	94.6	655	32.0
	88.5	92,0	650	31.1
Average and standard deviation	89.2 ± 0,7	89.8 ± 3.5	655 ± 5	30.4 ± 1.2
MS-OR(44.96%U)			648	32.2
			656	32.1
MS-L(6.92%U)			653	30.7
			630	30.0
MS-VL(3.08%U)			657	30.6
			665	32.8
			652	28.0
			671	29.0
NBS(1.0%U)			660	31,6
			657	30.6
Average and standard deviation			655 ± 11	30.8 ± 1.5

Table 4.--Experimental alpha activity constants for Rn^{222} determination.

Efficiency calculated from ZnS sources (percent)	Standard counting rates (c/min/mg equivalent)	
	Calculated from efficiency	Frozen ore standards
19.7	145	148
21.6	159	147
19.3	142	148
20.2	149	143
20.4	150	144
20.0	147	150
19.6	144	
20.7	152	
20.4	150	
19.7	145	
20.3	149	
20.0	147	
20.1	148	
Average and standard deviation 20.1 ± 0.6	148 ± 4	147 ± 3

Sample	Rn^{222} content of standard pitchblende ore sample (percent equivalent)	Fraction of Rn^{222} equilibrium
MS-OR(44.96%U)	42.6	0.948
	43.2	0.961
GS-64(73.46%U)	68.0	0.926
	70.5	0.960
	66.9	0.912
MS-L(6.92%U)	6.51	0.941
MS-VL(3.08%U)	2.91	0.944
	2.95	0.957
NBS(1%U)	0.95	0.95
	0.93	0.93

of its equilibrium content due to retention of more radon, it is immersed in liquid nitrogen for 12 to 14 days. As radon is frozen in the ore sample, greater than 99 percent equilibrium will be attained with the radium. The freezing point of radon is -110° C whereas the liquid nitrogen temperature is -196° C. The sample is removed from its freezing environment, and a regular Rn^{222} analysis initiated immediately. The counting rate obtained is the standard counting rate of Rn^{222} and is compared to that obtained from the efficiency calculation in table 4. Table 4 also lists the Rn^{222} analyses of several standard ore samples at room temperature. The fraction of Rn^{222} in partial equilibrium with the Ra^{226} is calculated showing the magnitude of the Rn^{222} loss at room temperature.

Measurement of Pb^{210}

The separation and measurement of Pb^{210} is performed as previously described (Rosholt, 1954). The assumption is made that 138 day half-life Po^{210} will be in equilibrium with Pb^{210} in geological samples, and the determination of the alpha activity of Po^{210} will be used to calculate the Pb^{210} content.

Efficiency calculation and standardization of Pb^{210} measurement.--A 50-ml solution of radioactively pure Pb^{210}-Bi^{210}-Po^{210} containing approximately 5×10^{-8} curie of Po^{210} is adjusted to a pH of 2 to 3. One-hundred-fifty milligrams of zinc sulfide is added to the solution. Greater than 99 percent of the bismuth and polonium isotopes will be adsorbed on the zinc sulfide. The slurry is filtered, washed, and dried. Small fractions of this active zinc sulfide, representing approximately 3000-5000 alpha particle disintegrations per minute, are prepared and counted in the same manner as described for the preceding nuclides. The counting rate is calibrated to total alpha particle disintegration rate using the appropriate efficiency correction factor for the phototube used.

The active zinc sulfide is transferred to a nickel crucible, 4 grams of Na_2O_2 added, and the sample carefully fused to almost red heat. Some Po^{210} will easily volatilize from the zinc sulfide and crucible if not continually in intimate contact with the Na_2O_2 flux while being heated. The normal Pb^{210} analysis is performed on the source, determining the counting rate of the Po^{210} in the Bi_2S_3 precipitate. The ratio of the counting rate of the Po^{210} in the Bi_2S_3 precipitate to the total alpha particle disintegration rate calculated on the zinc sulfide source is the over-all efficiency value for the Pb^{210} determination. The standard counting rate of Pb^{210} is calculated from this efficiency value (calculation 9).

Table 5 shows both of these values along with Pb^{210} analyses on several standard ore samples. The ratio of the equivalent Pb^{210} content to the equivalent Ra^{226} content is calculated, thus indicating the magnitude of the Rn^{222} loss from the samples over a period of several years.

Measurement of Th^{232}

The $ZnS \cdot BaSO_4$ precipitate prepared for the Th^{232} analysis initially will contain the alpha emitters Ra^{224}, Rn^{220}, and Po^{216}. The Bi^{212} and Po^{212} activity will begin to build up as the Pb^{212} builds up. The time at which the activity starts to increase is the time when the zinc sulfide used to adsorb the originally present Pb^{212}-Bi^{212} was filtered from the solution.

The precipitate is measured in the same manner described for the preceding nuclides. The observed counting rate is corrected to obtain the peak counting rate that Ra^{224} and its daughter products would have from figure 4. The calculation of the fraction of Ra^{224} built up from zero activity from Th^{228} is

Table 5.--Experimental alpha activity constants for Pb^{210} determination.

Sample	Efficiency (percent)	Standard counting rate (c/min/mg equivalent)
ZnS source	26.9	198
	26.4	194
	27.1	199
	27.3	200
	26.8	197
	26.7	196
	26.8	197
	26.5	195
	27.3	200
	27.0	198
Average and standard deviation	26.8 ± 0.3	197 ± 2

Sample	Pb^{210} content of standard pitchblende ore sample (percent equivalent)	Fraction of Pb^{210} equilibrium
MS-OR(44.96%U)	42.8	0.953
	42.6	0.948
	42.0	0.934
GS-64(73.46%U)	70.2	0.957
	69.6	0.948
	68.4	0.945
MS-L(6.92%U)	6.41	0.927
MS-VL(3.08%U)	2.83	0.919
	2.88	0.935
	2.86	0.929
	2.89	0.939
NBS(1%U)	0.96	0.96
	0.96	0.96

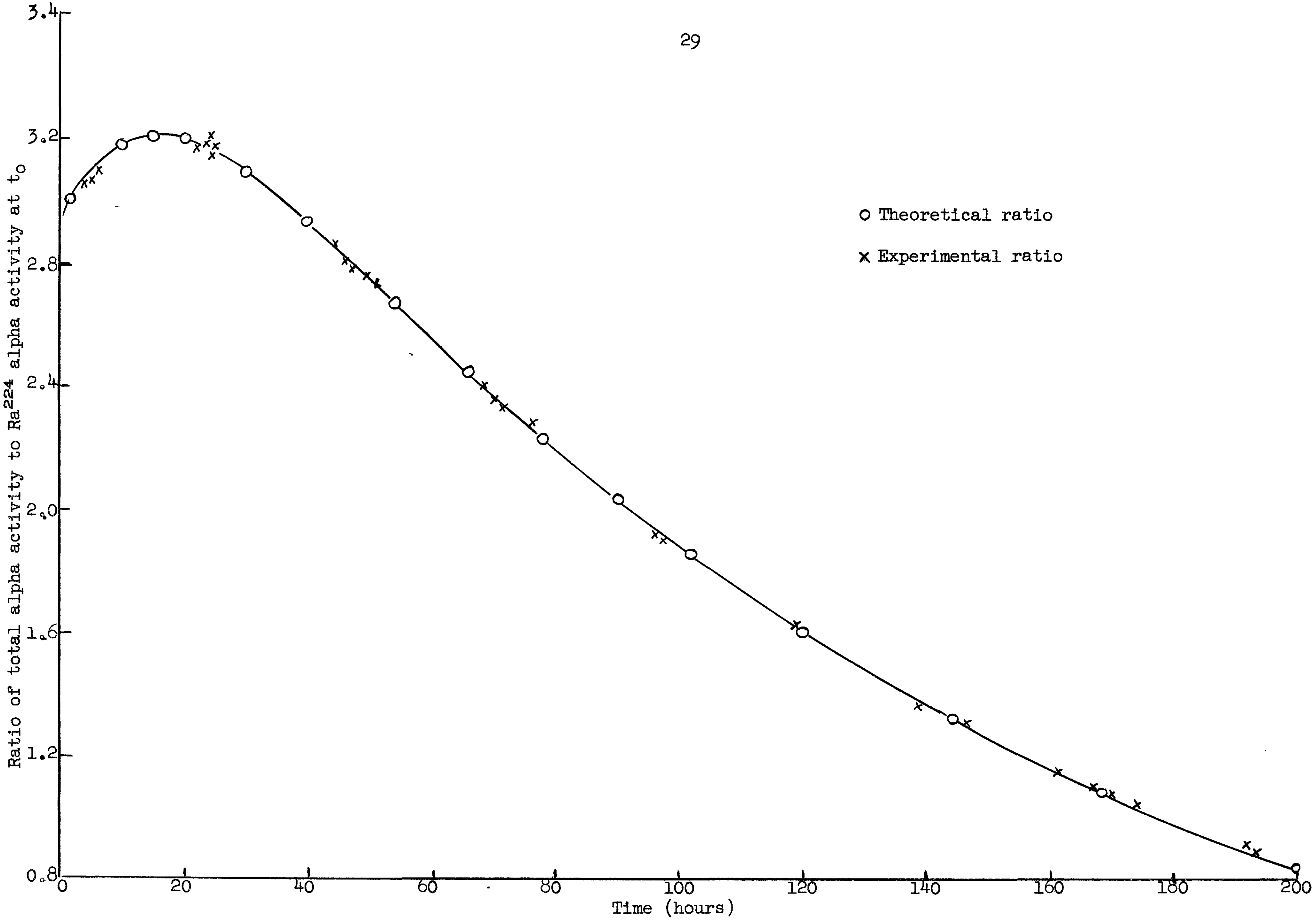

Figure 4.--Build-up and decay curve of Ra^{224}.

performed knowing the time elapsed between the first thorium separation and the second thorium separation isolating the Ra^{224} (calculation 11). The corrected counting rate of the sample would be the peak counting rate that Ra^{224} and its products would have at equilibrium with the Th^{228}.

Correction should be made for the contribution of Ra^{223} and its daughter products in the U^{235} decay series if the sample has an appreciable uranium content as the separation of Ra^{223} is identical to that of Ra^{224}. An analysis of the uranium content of the sample is usually available before the thorium determination is undertaken. Uranium series equilibrium and the theoretical ratio of U^{235} to U^{238} is assumed. In the time allowed for the Ra^{224} build-up, no measureable Ra^{226} will build up from the Th^{230} accompanying the Th^{232}-Th^{228}. The restrictions on the radium isotope contamination are limited to samples where the uranium-to-thorium ratio is not in excess of approximately 5 to 1. At present the lower analytical limit where this ratio is low is approximately 1 microgram of Th^{232} contained in the sample.

Efficiency calculation and standardization of Th^{232} determination.--A $Th(NO_3)_4 \cdot 4H_2O$ reagent which is at least 1 month old is used as the source of the isotopes for this efficiency measurement. The reagent does not necessarily have to be in equilibrium with respect to Th^{232}-Ra^{228}-Th^{228}. Thirty to 50 milligrams of the reagent is used as the source of the isotopes for this efficiency measurement.

The reagent is dissolved in 25 ml of water and made up to an acidity of 0.6 N HCl and a temperature of 45° C. One-hundred and fifty milligrams of zinc sulfide is added to adsorb the Bi^{212}-Po^{212} isotopes quantitatively. The slurry is filtered, washed with 0.4 N HCl, washed with alcohol, mounted, and dried. The time of filtration is recorded. The counting rate of the active zinc sulfide is measured for several continuous intervals. The counting rates are extrapolated back to the time of filtration. This value is the alpha particle counting rate for Bi^{212}-Po^{212} and for Th^{228}.

Bi^{212}-Po^{212} is allowed to build up in the solution from which the zinc sulfide was filtered. Equilibrium of the Bi^{212} with Th^{228} can be assured when all of the Bi^{212}-Po^{212} activity in the precipitate has decayed. If the Po^{210} activity is in excess of 0.1 percent of the original Bi^{212}-Po^{212} activity, it should be subtracted from the latter.

The solution is made to 1.0 N HCl at 60° C and 1 ml each of the Bi_2O_3, $Pb(NO_3)_2$ and $FeCl_3$ solutions are added. A regular thorium analysis by coprecipitation of Bi^{212}-Po^{212} with Bi_2S_3 is performed. The filtrate from this separation is also carried through the procedure for thorium analysis by the measurement of Ra^{224} and its products.

The standard counting rate for Bi^{212}-Po^{212} activity adsorbed on 150 mg of zinc sulfide is determined by following exactly the same procedure of Bi^{212}-Po^{212} adsorption using several accurately weighed 20 to 30 mg portions of the 48-year-old thorium nitrate salt. These standard values and the average are shown in table 6. This average value of c/min/mg equivalent Bi^{212} is used in calculation 11 instead of the specific activity of Th^{232} because of the difficulty involved in the determination of the detection efficiency for the measurement of Bi^{212}-Po^{212} adsorbed on zinc sulfide.

The efficiencies and standard counting rates of the two methods are calculated (calculation 11). These efficiencies, standard counting rates, the counting rates of standard ore samples, and a 48-year-old equilibrium $Th(NO_3)_4 \cdot 4H_2O$ reagent are shown and compared in table 6.

Table 6.--Experimental alpha activity constants for Th^{232} determination.

Sample	Efficiency (percent)		Standard counting rate (c/min/mg Th^{232})	
	Bi^{212}-Po^{212} measurement	Ra^{224} plus decay product measurement	Bi^{212}-Po^{212} measurement	Ra^{224} plus decay product measurement
ZnS source	12.0	295	26.0	638
	11.9	295	25.8	638
	12.0	293	25.9	634
	12.1	285	26.2	617
	11.8	284	25.5	615
	11.7	301	25.3	651
	11.9	303	25.8	656
	12.1	303	26.2	656
	11.8	295	25.5	638
	11.7	293	25.3	634
Average and standard deviation	11.9 ± 0.15	295 ± 7	25.8 ± 0.3	638 ± 14
1906 thorium nitrate salt (41.42% Th)			25.8	654
			25.9	618
			25.9	646
			25.9	628
			25.8	638
NBS(1.0% Th)			26.2	632
			25.6	635
			25.8	650
			26.0	620
			26.2	640
Average and standard deviation			25.9 ± 0.2	636 ± 12

Sample	Standard counting rate of Bi^{212}-Po^{212} on ZnS (c/min/mg equivalent Bi^{212})
1906 thorium nitrate salt (41.42% Th)	214.8
	215.8
	218.3
	214.6
	217.2
	214.0
	219.3
	218.6
	217.1
	214.2
Average and standard deviation	216.4 ± 2.0

CALCULATIONS

The decay constants used are taken from (Flanagan and Senftle, 1954):

1. Specific activities of uranium isotopes and equivalent amounts of each decay product (Kovarik and Adams, 1955):

Specific activity of U^{238} = 739.9 dis/min/mg U^{238}.

Activity of U^{238} in U of normal isotope abundance = (739.9 dis/min/mg)(0.99285)

= 734.6 c/min/mg U.

Activity of U^{235} = (734.6 c/min/mg U)(0.046) = 33.8 dis/min/mg U.

2. Specific activity of Ra^{226} and equivalent amounts of each decay product:

$$N\lambda = \frac{(6.0250 \times 10^{23} \text{ atoms})}{(226.1 \text{ g})} (10^{-9} \text{ g})(8.1252 \times 10^{-10}/\text{min}^{-1})$$

$$= 2165 \text{ dis/min}/10^{-9} \text{ g } Ra^{226}.$$

$$\frac{739.9 \text{ dis/min/mg } U^{238}}{2165 \text{ dis/min}/10^{-9} \text{ g } Ra^{226}} = 0.3417 \times 10^{-9} \text{ g } Ra^{226}/\text{mg } U^{238}.$$

Amount of Ra^{226} in U of normal isotope abundance $= \dfrac{734.6 \text{ dis/min/mg U}}{2165 \text{ dis/min}/10^{-9} \text{ g } Ra^{226}}$

$= 0.3393 \times 10^{-9}$ g Ra^{226}/mg U.

3. Specific activity of Th^{232} and equivalent amounts of each decay product:

$$N\lambda = \frac{(6.0250 \times 10^{23} \text{ atoms})}{(232.1 \text{ g})} (10^{-3} \text{ g } Th^{232})(9.481 \times 10^{-17}/\text{min}^{-1})$$

$$= 246.1 \text{ dis/min/mg } Th^{232}.$$

4. Function of Th^{227}: (Values used for the symbols in the equations are taken from Kirby, 1954, tables 15, 18, 20, 21).

Total alpha activity/initial alpha activity

$$= \frac{\alpha_{Pa^{231}}}{N_{Pa^{231}} \lambda_{Pa^{231}}} + 0.988 \frac{\alpha_t}{N_o \lambda_{Th^{227}}} + \frac{\alpha_t}{N_o \lambda_{Ac^{227}}} + \epsilon^{-\lambda_{Pb^{211}} t}.$$

$$= 1.0 + 0.988 \frac{\alpha_t}{N_o \lambda_{Th^{227}}} + \frac{\alpha_t}{N_o \lambda_{Ac^{227}}} + \epsilon^{-\lambda_{Pb^{211}} t}.$$

5. Function of Ra^{226}; (Kirby, 1954, tables 12, 21).

Total alpha activity/initial alpha activity $= \dfrac{\alpha_t}{N_o \lambda_{Ra^{226}}}$.

6. Function of Ra^{223}:

Total alpha activity/initial alpha activity $= 3\epsilon^{-\lambda_{Ra^{223}}} + (1-\epsilon^{-\lambda_{Pb^{211}}t})\epsilon^{-\lambda_{Ra^{223}}t}$.

7. Function of Ra^{224}: (Kirby, 1954, table 7).

Total alpha activity/initial alpha activity $= \dfrac{\alpha_t}{N_0\ \lambda_{Ra^{224}}}$,

8. Ra^{226} activity from radon train analysis:

Ra^{226} (dis/min) = (2165 dis/min/10^{-9} g Ra^{226})(g of Ra^{226} x 10^{-9}).

$$\text{Detection efficiency} = \frac{Ra^{226}\text{ activity by scintillation measurement}}{Ra^{226}\text{ activity by radon train measurement}}.$$

9. Efficiency and standard counting rate of Th^{230}, Pa^{231}, Ra^{226}, Ra^{223}, and Pb^{210} determinations:

$$\text{Efficiency} = \frac{\text{(activity of nuclide in carrier precipitate/detection efficiency)(10}}{\text{(activity of nuclide in ZnS source/detection efficiency)}}$$

S.C.R.(Th^{230}, Ra^{226}, Pb^{210}) = (efficiency)(734.6 dis/min/mg U)

= dis/min/100 mg of 1% equivalent.

S.C.R.(Pa^{231}, Ra^{223}) = (efficiency)(33.8 dis/min/mg U)

= dis/min/100 mg of 1% equivalent.

10. Efficiency and standard counting rate of Rn^{222} determination: Efficiency

$$= \frac{\text{(activity of } Po^{214} \text{ in } Bi_2S_3 \text{ precipitate)(detection efficiency)(100\%)}}{\text{(activity of } Ra^{226}, Rn^{222}, Po^{218}, Po^{214} \text{ - activity of } Ra^{226}) \text{ in ZnS source}} \text{ x } \frac{\text{activity of } Rn^{222}, Po^{218}, Po^{214}}{\text{activity of } Rn^{222}}.$$

S.C.R. = (efficiency)(734.6 c/min/mg U) = c/min/100 mg of 1% equivalent.

11. Efficiency and standard counting rates of Th^{232} determination:

$$\text{Efficiency } (Bi^{212}, Po^{212}) = \frac{\text{(activity of } Bi^{212}, Po^{212} \text{ in } Bi_2S_3 \text{ precipitate)}}{\text{(activity of } Bi^{212}, Po^{212} \text{ in ZnS source)}},$$

Efficiency (Ra^{224})

$$= \frac{\text{(peak activity of } Ra^{224}, Rn^{220}, Po^{216}, Bi^{212}, Po^{212} \text{ in } BaSO_4 \text{ precipitate)}}{\text{(activity of } Bi^{212}, Po^{212} \text{ in ZnS source)}(1-\epsilon^{-7.934 \text{ x } 10^{-3}t})}.$$

S.C.R. = (efficiency)(216.4 c/min/mg equivalent Bi^{212}) = c/min/100 mg of 1% Th^{232}.

DISCUSSION

In many geochemical problems it is desirable to have a quantitative measure of the amount of disequilibrium in a radioactive ore or rock. In any radioactive age method using lead isotopes it is necessary to know the state of equilibrium of a given sample. The Pb^{210} content in the sample is especially important in order to obtain a measure of the radon loss extending back over an interval of several years. The comparison of the Pb^{210}, the Rn^{222}, and the Ra^{226} contents is of primary importance in the evaluation of the validity of an age determination by the Pb^{210} method (Houtermans, 1951; Kulp and others, 1953). The Pb^{210} to Ra^{226} ratio in a recently collected unweathered specimen can be used to determine the emanating power of the specimen in its natural environment.

The comparison of the U^{238}, Th^{230}, Pa^{231}, and Ra^{226} contents may be very useful to the geologist attempting to determine the processes of weathering or alteration in the sample. Comparison of the ratios of the isotopes of radium or thorium may be helpful in the interpretation of geologic processes.

The possibility of developing a method of determining the ages of recent uranium deposits exists where the Pa^{231}/U and Th^{230}/U ratios are in good agreement and there is no indication of Ra^{226} or excessive Rn^{222} leaching. Ages ranging up to approximately 200,000 years could be determined where this method is applicable (Rankama, 1954).

Rapid methods for determining the Rn^{222}, Rn^{220}, and Po^{210} contents in clean water samples with very good sensitivity could be performed simply by adsorption of the polonium and bismuth isotopes on phosphorescent zinc sulfide powder in the same manner as in the determination of the efficiency of the Pb^{210} and thorium analyses.

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REFERENCES

Carney, R. J., and Campbell, E. D., 1914, A new method for the determination of thorium in monazite sand: Am. Chem. Soc. Jour., v. 36, p. 1136.

Curtiss, L. F., and Davis, F. J., 1943, A counting method for the determination of small amounts of radium or of radon: Natl. Bur. Standards Jour. Research (Research Paper RP1557), v. 31, p. 181-195.

Dalton, S. D., Golden, J., Martin, G. R., Mercer, E. R., and Thomson, S. J., 1953, Recent studies on iron meteorites III. Determination of uranium and thorium contents: Geochimica et Cosmochimica Acta, v. 3, p. 279.

Doerner, H. A., and Hoskins, W. J., 1925, Co-precipitation of radium and barium sulfates: Am. Chem. Soc. Jour., v. 47, p. 662-675.

Flanagan, F. J., and Senftle, F. E., 1954, Tables for evaluating Bateman equation coefficients for radioactivity calculations: Anal. Chemistry, v. 26, p. 1595-1601.

Houtermans, F. G., 1951, Über ein neues Verfahren zur Durchführung chemischer Altersbestimmungen nach der Blei-methode (A new procedure for chemical age determinations by the lead method): Akad. Wiss. Heidelberg, Math.-naturwiss. Kl., Sitzungsber., Abt. II, p. 123-126.

Kirby, H. W., 1954, Decay and growth tables for the naturally occurring radioactive series: Anal. Chemistry, v. 26, p. 1063-1071.

Kovarik, A. F., and Adams, N. I., Jr., 1955, Redetermination of the disintegration constant of U^{238}: Phys. Rev., v. 98, p. 46.

Kulp, J. L., Broecker, W. S., and Eckelmann, W. R., 1953, Age determination of uranium minerals by the Pb^{210} method: Nucleonics, v. 11, no. 8, p. 19-21.

Rankama, K., 1954, Isotope geology, New York, McGraw-Hill Book Co., p. 408.

Rosholt, J. N., Jr., 1954, Quantitative radiochemical method for determination of major sources of natural radioactivity in ores and minerals: Anal. Chemistry, v. 26, p. 1307-1311.