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A QUANTITATIVE RADIOCHEMICAL METHOD FOR THE DETERMINATION OF THE MAJOR SOURCES OF NATURAL RADIOACTIVITY IN ORES AND MINERALS

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CHEMISTRY

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A QUANTITATIVE RADIOCHEMICAL METHOD FOR THE DETERMINATION OF THE MAJOR SOURCES OF NATURAL RADIOACTIVITY IN ORES AND MINERALS

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ABSTRACT

The determination of Th^{232}, Rn^{222}, and Pb^{210} by isolation and subsequent activity analysis of some of their short-lived daughter products is described. The sulfides of bismuth and polonium are precipitated out of solutions of thorium or uranium ores, and the alpha particle activity of Po^{214}, Po^{212} and Po^{210} is determined by scintillation counting techniques. Po^{214} activity is used to determine Rn^{222}, Po^{212} activity for Th^{232}, and Po^{210} for Pb^{210}.

INTRODUCTION

The amount of natural radioactivity in an ore sample is determined in most laboratories by measuring the relative intensity of the beta-gamma radiations with a Geiger-Mueller counter. This amount of radioactivity determined under standardized conditions is compared with a standard uranium source measured under identical conditions and is usually reported as equivalent uranium (percent eU).

This determination of radioactivity of a sample is very useful but does not identify the source of this activity. The determination of equivalent uranium and uranium in a given sample may differ considerably due to lack of equilibrium in the radioactive series, to the presence of radioactive isotopes other than uranium and its equilibrium amounts of disintegration

products, and to statistical deviation of the analytical processes. When this difference is greater than that expected from the precision of either method or the combination of both, the reason for such disagreement should be determined and explained. The purpose of this paper is to meet this need by describing radiochemical methods whereby the radioactivity due to a particular element or its immediate disintegration products may be determined separately.

The methods described are for the actual determination of Po^{210}, Po^{214}, Po^{212} and Ra^{226}.

Data are presented for the analysis of samples of radioactive ores of varying composition.

This work was completed as part of a program undertaken by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission. The author is indebted to the staff of the Geochemistry and Petrology laboratory in Denver for valuable suggestions and assistance in the course of this work and to F. E. Senftle and L. F. Rader, also of the Geological Survey, for reviewing the report and making many suggestions.

CLASSIFICATION OF NATURAL RADIOACTIVITY IN SEPARATE GROUPS

The radioactivity of an ore sample can be attributed to many isotopes occurring in nature: the uranium, thorium, and actino-uranium series, $potassium^{40}$, $lutecium^{176}$, $rhenium^{187}$, $rubidium^{87}$, $samarium^{152}$, and tin^{124}. In this paper the only elements considered as measurable contributors are those of the uranium series, the thorium series, and, where the total activity is low, $potassium^{40}$.

A radioactive series decays successively from one isotope to another, each with its characteristic radiation. If equilibrium is established throughout the series then $\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \ldots$ where λ is the decay constant and N is the number of atoms. The subscripts refer to the parent element and each succeeding daughter. It is sometimes more convenient to express the above relationship in terms of half lives, $N_1/T_1 = N_2/T_2 = N_3/T_3 = \ldots$ where T is the half-life.

Even though a series is not in complete equilibrium, many of the immediate short-lived daughter products will be in equilibrium with their long-lived parent isotopes. Thus the two series can be separated into the major isotopes and groups of established equilibrium shown in figure 1 and listed below. The basic requirement for a group is that each daughter product will be in equilibrium with the parent of the group. In many cases radon will emanate from the ore, especially after it has been ground, resulting in a partial and continual loss of the radon group isotopes. Hence in the following list the radon group is not included with Ra^{226} under a heading of the radium group.

1. The uranium group consisting of U^{238}, Th^{234}, Pa^{234}, and U^{234}, where U^{238} is the long-lived parent ($T = 4.5 \times 10^9$ yr).

2. The $thorium^{230}$ isotope ($T = 8.0 \times 10^4$ yr).

3. The $radium^{226}$ isotope ($T = 1620$ yr).

4. The radon group consisting of Rn^{222}, Po^{218}, Pb^{214}, Bi^{214}, and Po^{214}, with radon the long-lived parent ($T = 3.825$ days).

5. The lead group containing Pb^{210}, Bi^{210}, and Po^{210}, with Pb^{210} the parent ($T = 22$ yr).

6. The $thorium^{232}$ isotope ($T = 1.39 \times 10^{10}$ yr).

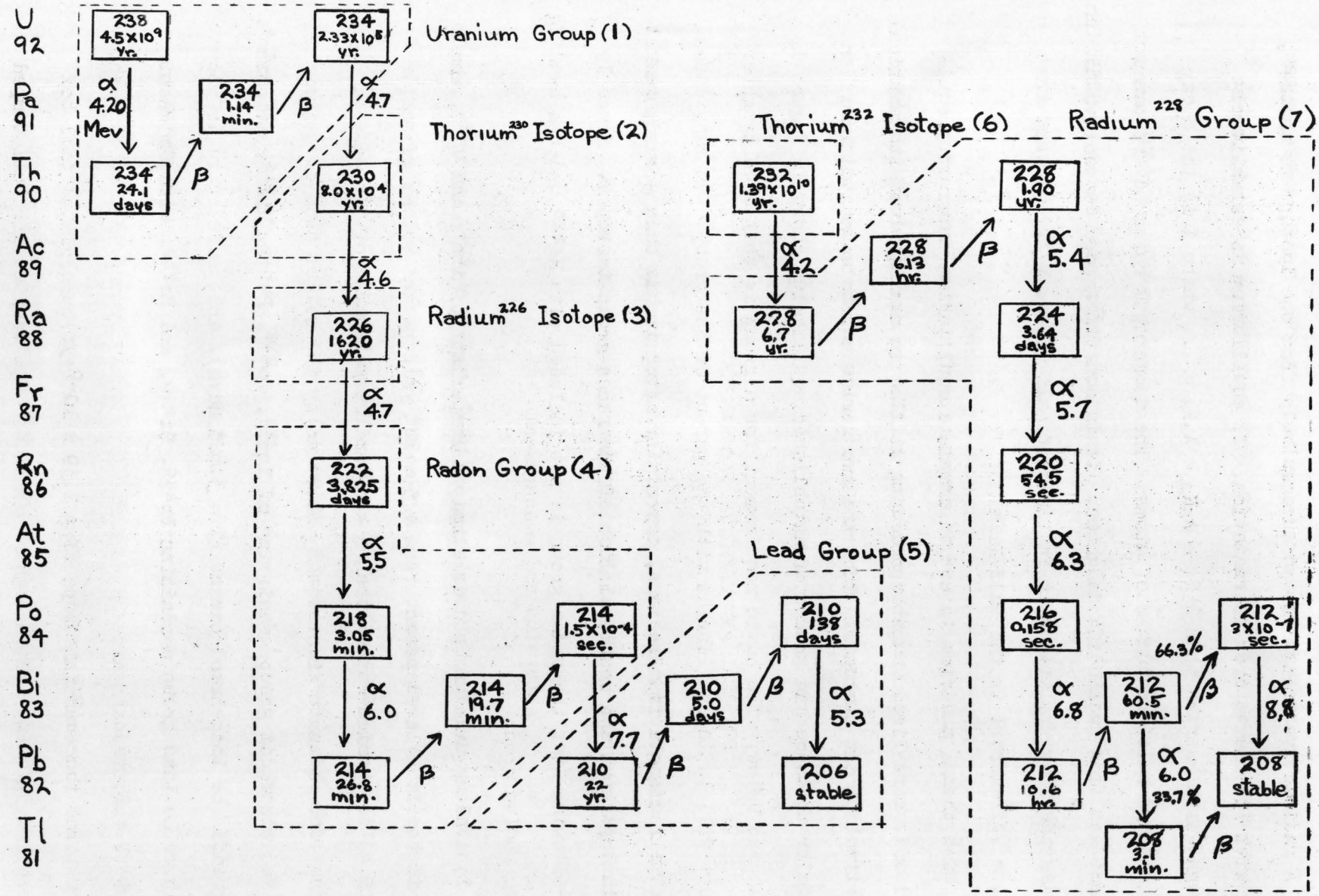

Figure 1.--Classification of natural radioactivity in separate groups

7. The radium^{228} group containing Ra^{228}, Ac^{228}, Th^{228}, Ra^{224}, Rn^{220}, Po^{216}, Pb^{212}, Bi^{212}, Po^{212}, and Tl^{208}, with Ra^{228} the long-lived parent (T = 6.7 yr).

Radiochemical methods for the determination of Th^{230} and Th^{232} are not included in this paper. It will be assumed that Th^{232} will be in equilibrium with the Ra^{228} group unless there is reason to believe otherwise and that the analysis of the latter will be valid for Th^{232}.

With these qualifying assumptions and the fact that intergroup equilibrium is established, then, according to the previously shown mathematical relationship, the quantities of the parent members may be calculated if one of its products can be determined.

PHYSICAL AND CHEMICAL PROCEDURES

The radioactivity due to all groups and isotopes is first determined by standard counting methods and calculated to percentage eU.

Apparatus and measurements

Equivalent uranium (eU) is simply a comparison of the count of a sample with the count of a standard uranium source. A constant volume of sample (12-20 g) is counted rather than a constant mass because of its ease of preparation. Because the activity detected by the Geiger tube is primarily beta radiation, it will not vary significantly with a large change in mass after infinite thickness is exceeded. An infinite thickness curve is shown in figure 2 with the beta-gamma activity plotted against the sample mass.

Both the standard and the samples, previously ground to pass 80 mesh, are prepared for counting by placing them in a half-ounce metal pill box (diameter 1 5/16 in. and thickness 5/8 in.). The samples are well tamped and smoothed off level with the top edge of the container.

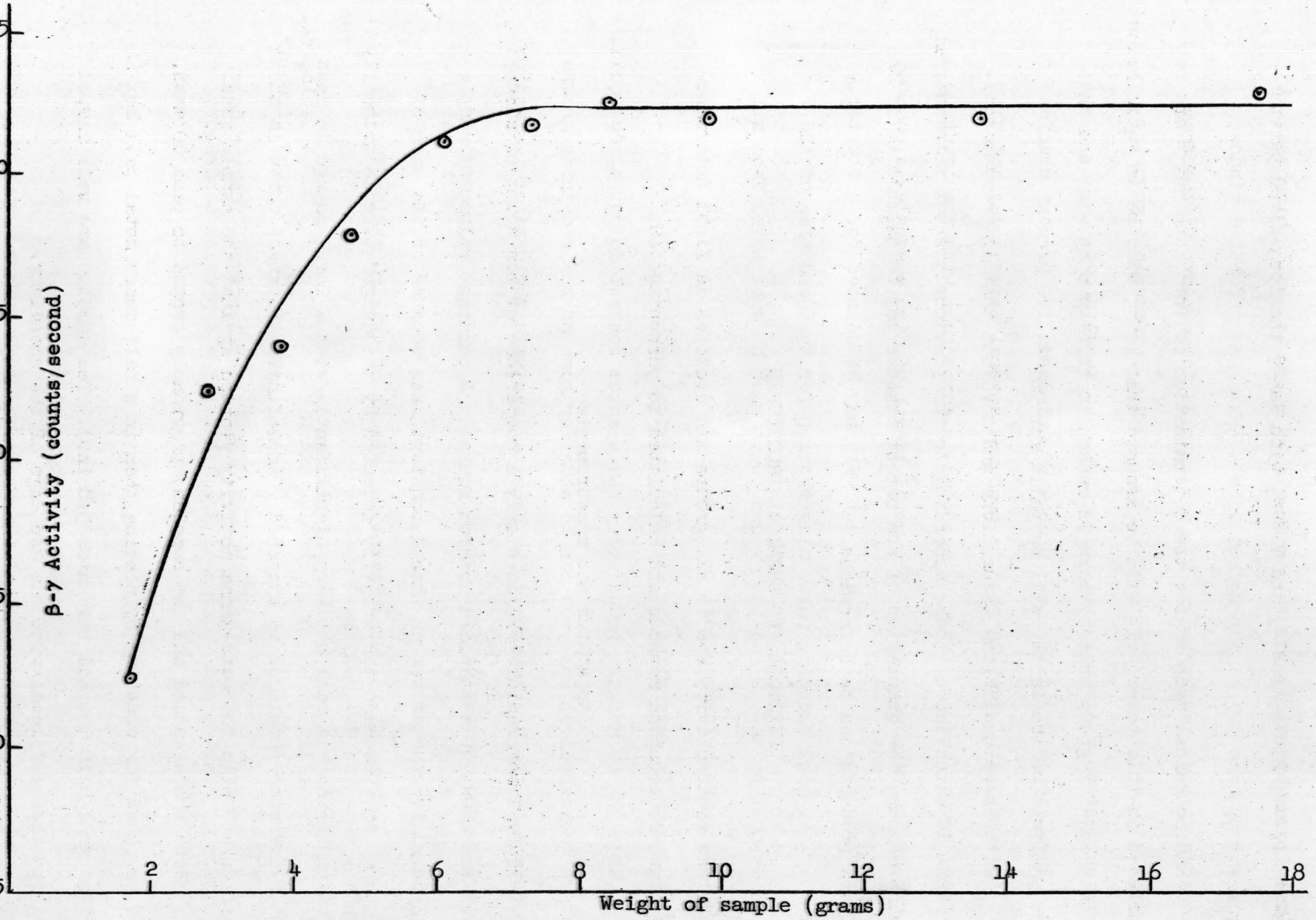

Figure 2.--Effect of sample mass on counting rate

The measurement is made by placing the sample directly underneath a mica-window Geiger tube in a lead shield of 1 1/2 in. wall thickness. A mica-window tube 2.5 to 3.3 mg/cm^2 with a 1 1/8 in. effective window diameter is used, supported by a stand notched for support of the tray containing the pill box to be measured. Thus a reproducible geometry with respect to the sample and the Geiger tube is attained.

As the standard a National Bureau of Standards 1.0 percent uranium ore is used. Its counting rate is measured several times a day and the average counts/second/percent U are used in comparison with the counting rates of the unknown sample. The usual length of time a sample is counted is five minutes. Samples of high activity may be counted for a shorter time.1/ At high counting rates a correction for the dead time of the counter must be made.2/ A background count must be subtracted from all counting rates before comparison is made.

Uranium is determined by standard chemical methods.3,4/

When the eU and the actual chemical uranium content do not agree, quantitative radiochemical analyses can be made for some of the remaining groups to determine the discrepancy. The chemical analysis for uranium is used to determine the content of that group.

1/ Kohman, T. P., Measurement techniques of applied radiochemistry: Anal. Chemistry, vol. 21, p. 361, 1949.

2/ Kohman, T. P., Op. cit., p. 357.

3/ Grimaldi, F. S., May, Irving, and Fletcher, Mary H., U. S. Geological Survey fluorimetric methods of uranium analysis, U. S. Geol. Survey Circular 199, 1952.

4/ Rodden, C. J., et al., Manual of analytical methods for the determination of uranium and thorium in their ores, New Brunswick Laboratory, September 1950.

A relatively simple analysis of certain isotopes can be used to determine which groups, relative to certain standards, produce the radioactivity inherent in a sample, and thus determine the source of disequilibrium in the sample.

The determination of the amounts of Po isotopes present is made by alpha-particle count with a scintillation detector, using silver-activated zinc sulfide phosphor placed on the sensitive area of a 5819 photomultiplier tube and covered with a thin aluminum foil. An appropriate aluminum absorber is used between the precipitate and the detector when counting Po^{212} and Po^{214}. The thickness of this absorber is such that in combination with the built-in aluminum light shield on the detector, just enough absorption is created to prevent any 5.3 Mev alpha particles of Po^{210} from reaching the phosphor. The scintillation detector is calibrated to constant sensitivity by counting a standard source of Pb^{210} + Bi^{210} + Po^{210} (in equilibrium) with every determination, and comparing this count with that obtained from the same source when the Th^{232}, Rn^{222}, and Pb^{210} values were determined.

Solution of the sample

A 0.1- to 0.5-g sample, depending on total activity and ease of solution, is fused to red heat with 4 g of Na_2O_2 in a nickel crucible. It is important that approximately the same amount of flux and the same conditions of fusion be used for all samples in order to insure a more consistently uniform sulfide precipitation.

The time of fusion is recorded. The melt is taken up in water, neutralized carefully with concentrated HCl, then made up to an acidity of 1.0 normal with HCl and to a total volume of 100 ml. With this treatment the sample should be completely in solution. A few ores may not convert to a clear solution immediately; these will have to be allowed to stand for some time in order to

get them to dissolve. If solution is still not obtained or where radon analysis is desired and immediate resumption of procedure is necessary, a smaller sample may be tried. A smaller sample should also be used for ores that contain a very high percentage of silica so that there will be a more rapid filtration of the sulfides. To obtain a more uniform precipitate in the presence of niobium and tantalum or titanium, a small amount of sodium fluoride can be added.

Preparation of precipitate for determinations

To 1 ml of 0.016 molar Bi_2O_3 in 1.8 percent HCl solution (6 mg Bi) 1 ml of 0.014 molar $Pb(NO_3)_2$ solution (3 mg Pb) is added and the solution is gassed with H_2S for 10 minutes. The bismuth is used as a carrier of the polonium and bismuth isotopes. The lead is intended to dilute the coprecipitation of the radioactive lead isotopes.

The $(Bi,Po)_2S_3$ precipitate is filtered on a 7.0-cm no. 42 paper in a no. 0 Buchner funnel using a suction flask. The precipitate is washed to the center of the paper with water and the filtrate transferred to a 250-ml beaker. The sides of the paper are completely washed down with alcohol. The damp precipitate and paper are glued to an aluminum ring 1 7/8 in. in diameter and dried with moderate heat.

The time is recorded as the mean between the beginning of filtration and the time when the entire solution has passed through the filter paper. It is desirable that no more than 6 to 8 minutes be required for this operation.

This precipitate will contain the isotopes Po^{218}, Bi^{214}, Po^{214}, Bi^{210}, and Po^{210} when radium^{226} is present and Po^{216}, Bi^{212}, and Po^{212} when thorium^{232} is present. The amount of these isotopes present is determined by alpha-particle count with a scintillation detector.

The radon group (thorium series absent)

When a radon determination is desired, the foregoing preparation must be rapid. Between the time of fusion and precipitation of the radon group the controlling isotope is Pb^{214}, that is the radioactivity in the solution decays with a half-life of 26.8 minutes, the half-life of Pb^{214}, as radon itself was expelled during the fusion. It is desirable that no more than 30 minutes be used in this operation, and no more than 6 to 10 minutes additional time should elapse before the count is initiated. After precipitation the controlling isotope is Bi^{214} with a half-life of 19.7 minutes.

The count itself is made on the 7.68 Mev alpha particles emitted by Po^{214} ($T = 1.5 \times 10^{-4}$ seconds). At least three determinations of counting rate immediately following each other should be taken. A plot on semi-logarithmic graph paper is made of these counting rates against time to determine the radon content at the time of fusion. (See figure 3).

If no isotopes of the thorium series are present in the sample, the plot will be a straight line with the slope of decay curve of Bi^{214} ($T = 19.7$ min). This line is extrapolated back to time of precipitation. Another line is drawn with the slope of decay curve of Pb^{214} ($T = 26.8$ min) from the point of intersection of the Bi^{214} decay curve and the ordinate representing the time of precipitation to the ordinate representing the time of fusion. The final extrapolated point represents the activity of Pb^{214}, at the time of fusion. However, if one assumes that at this time there was equilibrium between Rn^{222}, Po^{218}, and Pb^{214}, the activity is the same for these three nuclides. This value of Pb^{214} is then compared with the count (obtained in the same manner) of a source of radon in equilibrium with a standard uranium

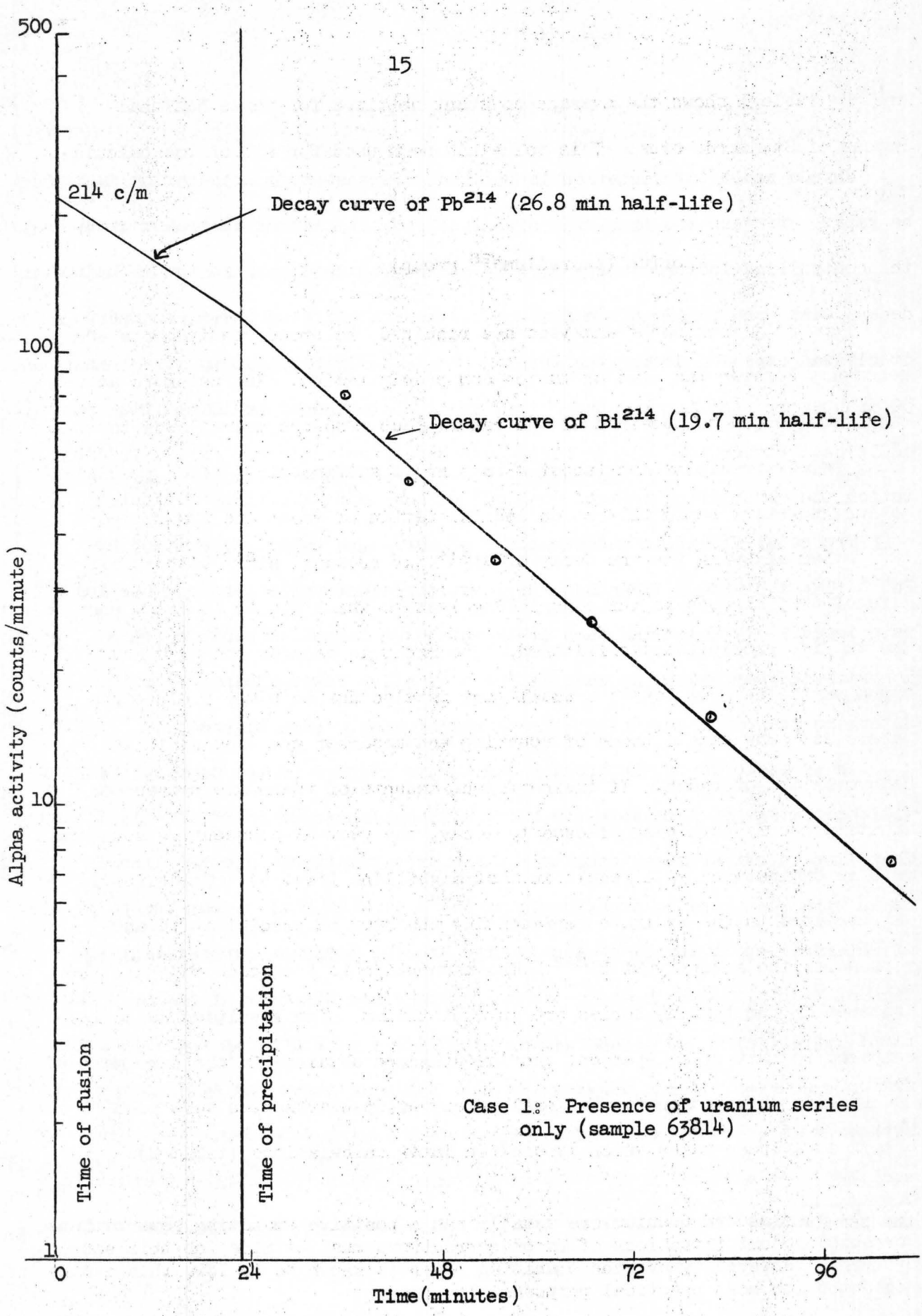

Figure 3.--Decay curve of Pb^{214} product alpha activity and decay curve of Bi^{214} through 5.1 mg/cm^2 aluminum absorber

ore.5/ Table 1 shows the average constant obtained for three National Bureau of Standards ores. This value has been used for all of the calculations.

Thorium (as radium^{228} group)

When only thorium^{232} analyses are required, no speed requirements are necessary between the time of fusion and precipitation. In fact more accurate results can be obtained if the radon group products are allowed to decay before precipitation (about 4 to 5 hr is sufficient). After precipitation, however, rapid filtration and initiation of count are desirable.

After allowing for the decay of Bi^{214}, if present, Bi^{212} with a half-life of 60.5 minutes is the controlling isotope which starts to decay when the sulfide precipitate is filtered. The count is made on the 8.78 Mev alpha particles from Po^{212}; a small part is also due to 6 Mev Bi^{212} alpha particles. The same methods of counting and absorber are used as in the determination of radon. If insignificant amounts of radon are present or if its products have been allowed to decay, the plot of consecutive counting rate determinations will result in a straight line (fig. 4). This line is extrapolated to the ordinate representing the time of precipitation and represents the activity of Bi^{212}. The assumption is then made that all the isotopes in the thorium series are in equilibrium. The resulting value is compared to that of a 1-percent thorium standard obtained in the same manner. The results obtained on two National Bureau of Standards ores were used to obtain an average value which is used in later calculations (table 2).

5/ A standard uranium ore usually has a positive emanating power. Hence for absolute determinations of radon corrections must be made for this source of error. However, where the emanating power is known to be low, this can be neglected for most practical purposes.

Table 1.--Experimental alpha activity constants of uranium series standards used in radiochemical determinations on 0.2500-g amounts of sample.

Sample	Counts/minute 10^{-9} curies Rn^{222}/g of sample	Counts/minute 10^{-9} curies Pb^{210}/g of sample
NBS 1 percent U	90.0	87.7
	89.5	85.1
	87.2	86.0
	90.3	82.2
NBS no. 2230-1 (MS-VL 3.08 percent U)	91.0	86.3
	85.3	83.4
	89.7	86.8
	91.0	83.6
	88.2	87.6
NBS no. 2230-2 (MS-L 6.92 percent U)	88.9	86.8
	94.7	88.5
	89.2	78.7
	88.0	80.0
	88.9	80.8
Average and standard deviation	89.4 $\pm$ 2.1	84.5 $\pm$ 3.1

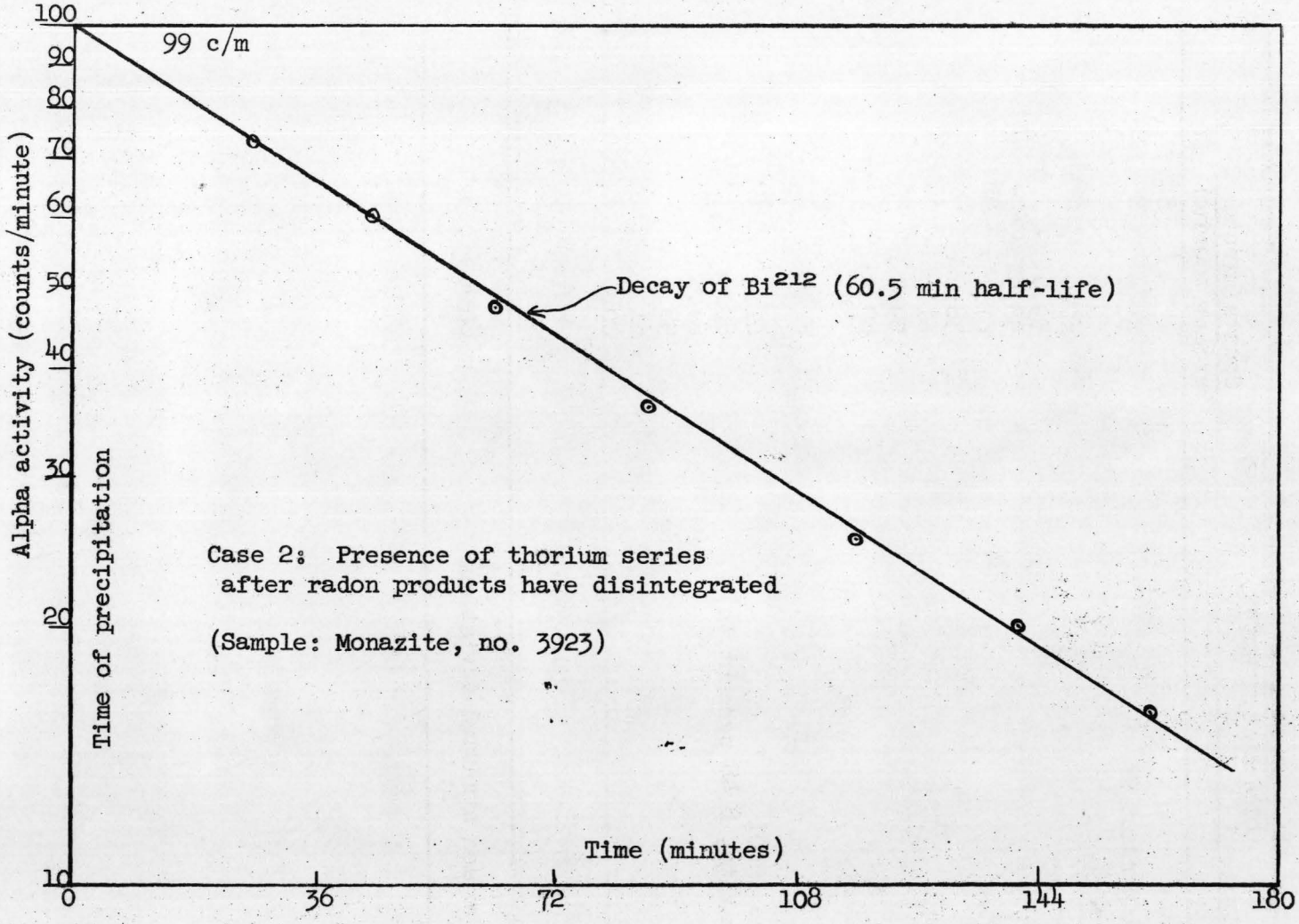

Figure 4.--Decay curve of Bi^{212} and product alpha activity through 5.1 mg/cm^2 aluminum absorber

Table 2.--Experimental alpha activity constants of thorium series standards used in radiochemical determinations on 0.2500-g amounts of sample.

Sample	Counts/minute / Percent thorium
NBS 1 percent Th	61.2
	59.5
	60.0
	59.6
	58.5
	61.1
	58.8
	61.0
	59.5
	60.0
NBS no. 2601 (Monazite, 8.48 percent Th)	61.0
	60.5
	64.5
	58.5
	61.6
	60.5
Average and standard deviation	60.4 ± 1.5

Combined radon and thorium analyses

In the presence of significant quantities of both radon^{222} and thorium^{232} products, the resulting curve of counting rate against time will describe initially a decay somewhere between Bi^{214} and Bi^{212}. As Bi^{214} decays to a small fraction of its initial value, the pure Bi^{212} decay curve will be defined. (See figure 5.) This Bi^{212} curve is extrapolated back to the ordinate representing the time of precipitation. The decay curve of Bi^{214} is obtained after subtracting the difference between the curve representing the Bi^{212} decay and the curve representing the combined decay of Bi^{212} and Bi^{214}. With these corrected and extrapolated points the quantities of Rn^{222} and Th^{232} can be determined as previously shown.

The lead^{210} group

The products of radon^{222} and thorium^{232} are allowed to decay for 1 day, and an alpha count is again made on the sulfide precipitate. In determining this count, no absorber is used and decay curves need not be drawn. Po^{210} with a half-life of 138 days is the emitter of the alpha particles counted and a wait of several days can be made with no correction required for its decay. This counting rate is then compared to a source of Po^{210} prepared in the same manner from a standard uranium ore. Table 1 contains the standard constants in these analyses.

Radium^{226}

The method of Curtiss and Davis 6/ is used to determine the radium content of an ore. The sample to be analyzed must be completely in solu-

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6/ Curtiss, L. F., and Davis, F. J., A counting method for the determination of small amounts of radium and radon: Nat. Bur. Standards Jour. Research, vol. 31, p. 181, 1943.

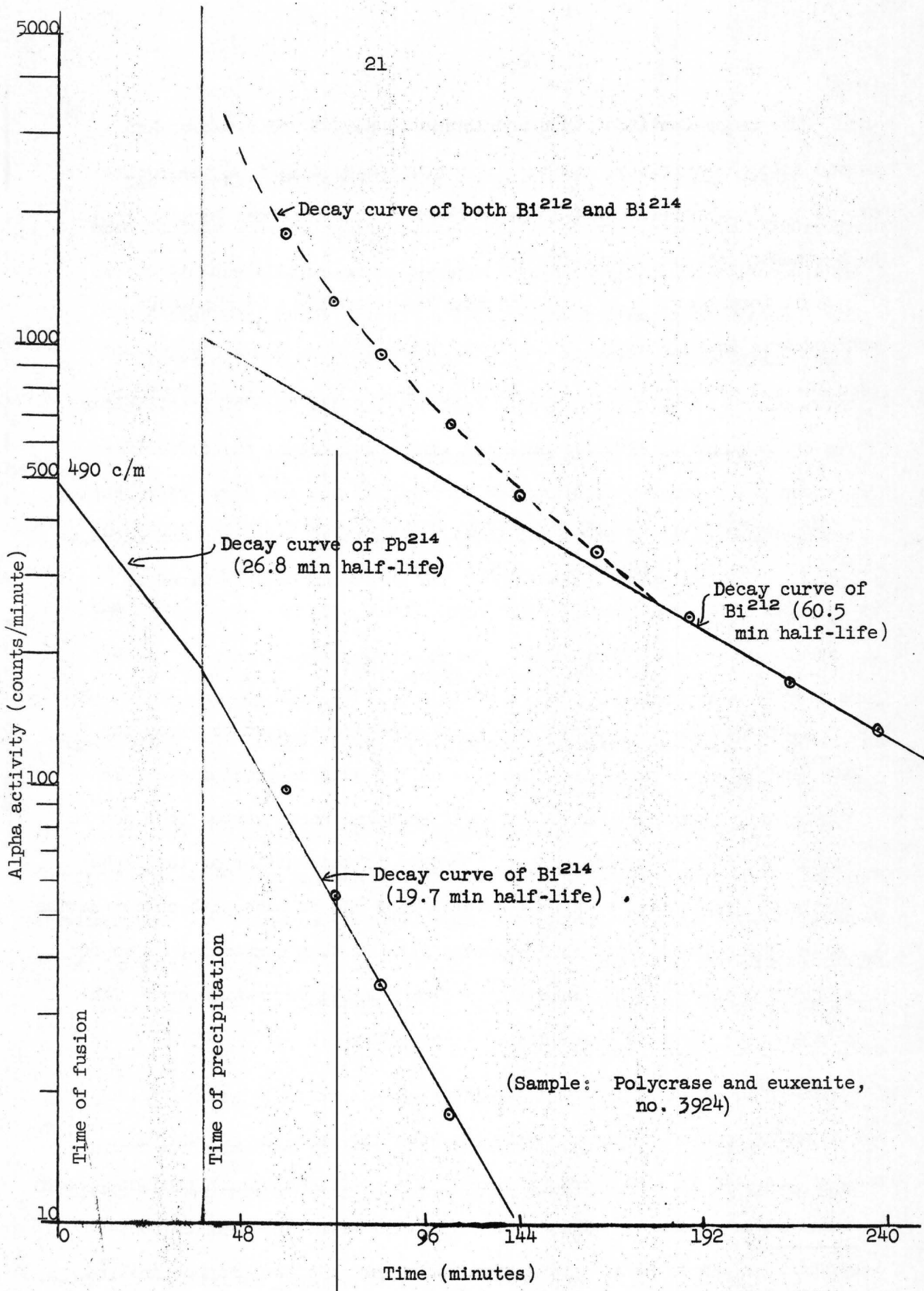

Figure 5.--Relationship of combined decay curve of Bi^{212}, Bi^{214} product alpha activity to the differentiated decay curves of Pb^{214}, Bi^{214}, Bi^{212} product activities

tion. The radon contained in the solution is boiled under vacuum and passed into an ionization chamber. The count resulting from the ionization of the gas in the chamber is compared to the count obtained from the radon in a standard radium solution of 10^{-9} g.

A different method of solution than that described in the above reference is usually used. A 0.1- to 1.0-g sample is fused with sodium peroxide and acidified to a 3 to 4 percent hydrochloric acid solution.

DISCUSSION OF UNITS AND EXPRESSION OF RESULTS

The thorium and uranium content is reported as an actual percent of thorium or uranium, respectively. The uranium content is also converted to curies x 10^{-9}/gram of sample and reported as such for comparison with the other amounts described below. The radiation from 1 gram of 1 percent pure U^{238} is equivalent to 3.42 x 10^{-9} curies. The content of Ra^{226}, Rn^{222}, and Pb^{210} is reported separately as curies of Ra^{226}, Rn^{222}, and Pb^{210} x 10^{-9} per gram of sample, respectively.

A curie is defined as that amount of radioactive material which will give 3.7 x 10^{10} disintegrations per second. A uranium sample in equilibrium with respect to the three isotopes listed above will contain the same number of curies of each of these isotopes. If the number of curies of any of the three isotopes is greater or less than the equilibrium amount, the excess or deficit represents the degree of disequilibrium.

The value of eU (equivalent uranium) is defined as the ratio of the net counting rate of a sample to the net counting rate per percent of a uranium standard in equilibrium with all of its disintegration products, both measured under similar geometry. Thus, it will equal the uranium content only when the sample is in equilibrium and other emitters are not present.

A useful check for the amounts of radon^{222}, lead^{210}, and thorium^{232} is based on the fact that the normal distribution of the isotope groups for a sample in equilibrium, measured in the Geochemistry and Petrology laboratory, Denver, with its conditions of geometry, is such that approximately 40 percent of the beta-gamma count is due to uranium^{238} and its products down to radium^{226}, about 40 percent is due to the products between radon^{222} and lead^{210}, and about 20 percent is due to lead^{210} and its daughter products.

When thorium^{232} in equilibrium with its decay products is present in a uraniferous sample, the measured beta-gamma activity is equal to the sum of the activities produced by the uranium^{238}, radon^{222}, and lead^{210} groups, plus the thorium^{232} activity. This latter activity is equivalent to the activity of an equilibrium uranium sample the uranium content of which is 20 percent of the thorium present in the sample.

Thus the sum of the equivalent beta-gamma activities of each group converted to percent will give a calculated value of equivalent uranium (eU_c).

$eU_c = \frac{(0.4)(U^{238})+(0.4)(Rn^{222})+(0.2)(Pb^{210})}{3.42}$ and, in the case of the presence of thorium $eU_c = \frac{(0.4)(U^{238})+(0.4)(Rn^{222})+(0.2)(Pb^{210})}{3.42} + \frac{(0.2)(\%\ Th^{232})}{1}$.

When U^{238}, Rn^{222}, and Pb^{210} are in curies x 10^{-9}/g of sample and Th^{232} in percent, eU_c should be approximately equal to the determined value of equivalent uranium.

EXPERIMENTAL DATA

Three National Bureau of Standards uranium ores were used to determine the values of detected alpha activity of Rn^{222} and Pb^{210} for 10^{-9} curies/g of sample, using the methods described for these determinations. Table 1 shows the value for each individual determination together with the average

values of $\frac{\text{counts/minute}}{10^{-9}\text{curies of } Rn^{222}/g \text{ of sample}}$ and $\frac{\text{counts/minute}}{10^{-9} \text{ curies } Pb^{210}/g \text{ of sample}}$, subsequently used as standards in the analysis of ores for these isotopes. The standard deviation of these average figures is also shown. It will be noted that the amounts of Rn^{222} and Pb^{210} in the standards differ slightly. These should be considered as two different amounts and not averaged together. This is due to the fact that there are different absorption factors in the measurement of each and that there is a variance in degree of sulfide precipitation between the two as shown in the section on Experimentally determined conditions.

Table 2 shows the Po^{212} alpha activity in $\frac{\text{counts/minute}}{\text{percent Th}}$ of two standard thorium ores from the National Bureau of Standards. The standard deviation for the average is shown.

Comparison of thorium analyses determined by proposed methods and those determined by classical chemical methods is given in table 3. Ores containing various thorium minerals were analyzed.

Analyses of various ore samples for U^{238}, Th^{232}, Ra^{226}, Rn^{222}, and Pb^{210} are given in table 4. The table is divided into groups where the majority of the radioactivity is due to thorium, excess radium, and deficient radium. Where the samples contain only the uranium series, the activities of each member of the series should be the same. These particular analyses clearly show disequilibrium, the seriousness of which can be seen from the activities of the four daughter products shown.

Table 5 illustrates the comparison of eU determined by beta-gamma counting methods and eU_c (calculated) as the summation of the counts of each component group. The results shown an agreement within the limits of error of such methods.

Table 3.--Comparison of chemical and radiochemical thorium determinations of various thorium ores and minerals

No. and sample	Percent thorium Chemical analysis 1/	Percent thorium Radiochemical analysis
3926 Aeschynite	5.74 5.54	5.76 5.50
3924 Polycrase and euxenite	4.43 4.60	4.55 4.56 4.32 2/
3923 Monazite	4.21 4.23	4.13 3.92
A 13 Black sand	3.12 3.29	3.12 3.26 3.11
A 26 Black sand	1.67 1.79	1.75 1.82
3181 Ward's thorianite	2.74 2.86	3.02 2.94
3063 Thorianite	1.75 1.65	1.74 1.74 1.72
3905 Thorite	1.68 1.58	1.09 1.07 1.25 1.20 1.10

1/ Chemical analyses by Harry Levine, U. S. Geological Survey.

2/ Rn^{222} and Pb^{210} for this sample: $\frac{13.7 \times 10^{-9} \text{ curies } Rn^{222}}{\text{g of sample}}$ and $\frac{13.4 \times 10^{-9} \text{ curies } Pb^{210}}{\text{g of sample}}$.

Table 4.--Analysis of miscellaneous ore samples for U^{238}, Ra^{226}, Rn^{222}, Pb^{210}, and Th^{232}.1/

Sample no.	U (in percent)	Th (in percent)	U^{238} (in curies x 10^{-9}/g of sample)	Ra^{226} (in curies x 10^{-9}/g of sample)	Rn^{222} (in curies x 10^{-9}/g of sample)	Pb^{210} (in curies x 10^{-9}/g of sample)
Samples containing thorium						
52336	0.005	1.2	0.02	0.034		
52337	0.002	0.41	0.007	0.02		
63526	0.010	0.44	0.034	0.092	0.2	0.1
63527	0.005	0.06	0.02			
63528	0.008	0.15	0.03	0.02	0.07	0.1
67150	0.001	7.1	0.003			0.03
Samples with deficient radium^{226}						
63814	19.9		68.0	8.82	4.70	7.05
64124	0.45		1.5	1.2	0.75	0.41
64125	0.48		1.6	1.6	1.1	0.62
Samples with excess radium^{226}						
64123	0.10		0.34	5.88	4.8	4.4
64126	0.008		0.03	1.7	1.6	1.0
64128	0.13		0.44	19.8	17.	17.
64129	0.14		0.48	5.91	4.8	4.8
64130	0.17		0.58	2.9	2.5	2.7
64131	0.009		0.03	0.72	0.51	0.68
64132	0.005		0.02	2.2	1.9	1.2
64133	0.064		0.22	1.9	1.5	1.2
64630	0.036		0.12	0.61	0.54	0.34
64631	0.034		0.12	0.85	0.61	0.44

1/ Uranium analyses by the staff of the Geochemistry and Petrology Branch Denver laboratory.

Table 5.--Comparison of calculated and determined eU used for checking.1/

1 Sample no.	2 (0.4 U)	3 (0.4 Rn)	4 (0.2 Pb)	5 (0.2) x % Th	eU_c 2/	eU determined by β-γ count
52336	0.008	0.014	0.007	0.24	0.25	0.23
52337	0.003	0.008	0.004	0.082	0.085	0.084
63526	0.014	0.08	0.02	0.088	0.12	0.13
63527	0.008			0.012	0.01	0.021
63528	0.01	0.03	0.02	0.030	0.05	0.041
63814	27.2	1.88	1.41		8.9	8.7
64123	0.14	1.9	0.88		0.85	0.84
64124	0.60	0.30	0.082		0.29	0.30
64125	0.64	0.44	0.12		0.35	0.36
64126	0.01	0.64	0.20		0.25	0.23
64128	0.18	5.6	3.4		2.8	2.9
64129	0.19	1.9	0.96		0.89	0.90
64130	0.23	1.0	0.54		0.52	0.50
64131	0.01	0.20	0.14		0.10	0.10
64132	0.008	0.76	0.24		0.29	0.26
64630	0.048	0.22	0.068		0.098	0.088
64631	0.048	0.24	0.088		0.11	0.12
67150	0.001	0.01	0.01	1.4	1.4	1.4

1/ U, Rn, and Pb are in curies x 10^{-9}/g sample; Th is in percent.

2/ $eU_c = \frac{(\text{cols. } 2+3+4)}{3.42} + \text{col. } 5.$

The results are calculated from the following formulas:

$$\text{Th (\%)} = \frac{(\text{Po}^{212}\text{ alpha activity, c/m}) \left(\frac{0.250\text{ g}}{\text{mass of sample}}\right)\left(\frac{1430}{K}\right)}{60.4\text{ c/m/ \% Th}}$$

$$\text{Rn}^{222}\ (10^{-9}\text{ curies/g of sample}) =$$

$$\frac{(\text{Po}^{214}\text{ alpha activity c/m}) \left(\frac{0.250\text{ g}}{\text{g of sample}}\right)\left(\frac{1430}{K}\right)}{89.4\text{ c/m/}10^{-9}\text{ curies Rn}^{222}\text{/g of sample}}$$

$$\text{Pb}^{210}\ (10^{-9}\text{ curies/g of sample}) =$$

$$\frac{(\text{Po}^{210}\text{ alpha activity c/m}) \left(\frac{0.250\text{ g}}{\text{g of sample}}\right)\left(\frac{1430}{K}\right)}{84.5\text{ c/m/}10^{-9}\text{ curies Pb}^{210}\text{/g of sample}}$$

where the denominators are the counting rates for 0.250 g of the particular standard in question.

The value 1430 $\pm$ 14 c/m is a standard calibration constant of a Po source and K is the sensitivity standard value obtained at the time of the determination to correct the detector to standard conditions. For example from figure 3: (0.125 g sample of 63814)

$$\frac{(214\text{ c/m})\ \frac{(0.250)}{(0.125)}\ \frac{(1430)}{(1460)}}{89.4\text{ c/m/}10^{-9}\text{ curies Rn}^{222}\text{/g}} = \frac{4.70 \times 10^{-9}\text{ curies Rn}^{222}}{\text{g of sample}}$$

EXPERIMENTALLY DETERMINED CONDITIONS FOR PROCEDURE

The optimum amount of carrier to be used was determined experimentally and shown in figure 6.

The critical acidity curves for the precipitation of Po^{210}, Bi^{214}, and Bi^{212} are shown in figures 7, 8, and 9, respectively. The precipitation in both the presence and absence of a sodium peroxide fusion is described. The use of the sodium peroxide fusion on the sample lowers the acidity required for the proper precipitation of the bismuth and polonium sulfides.

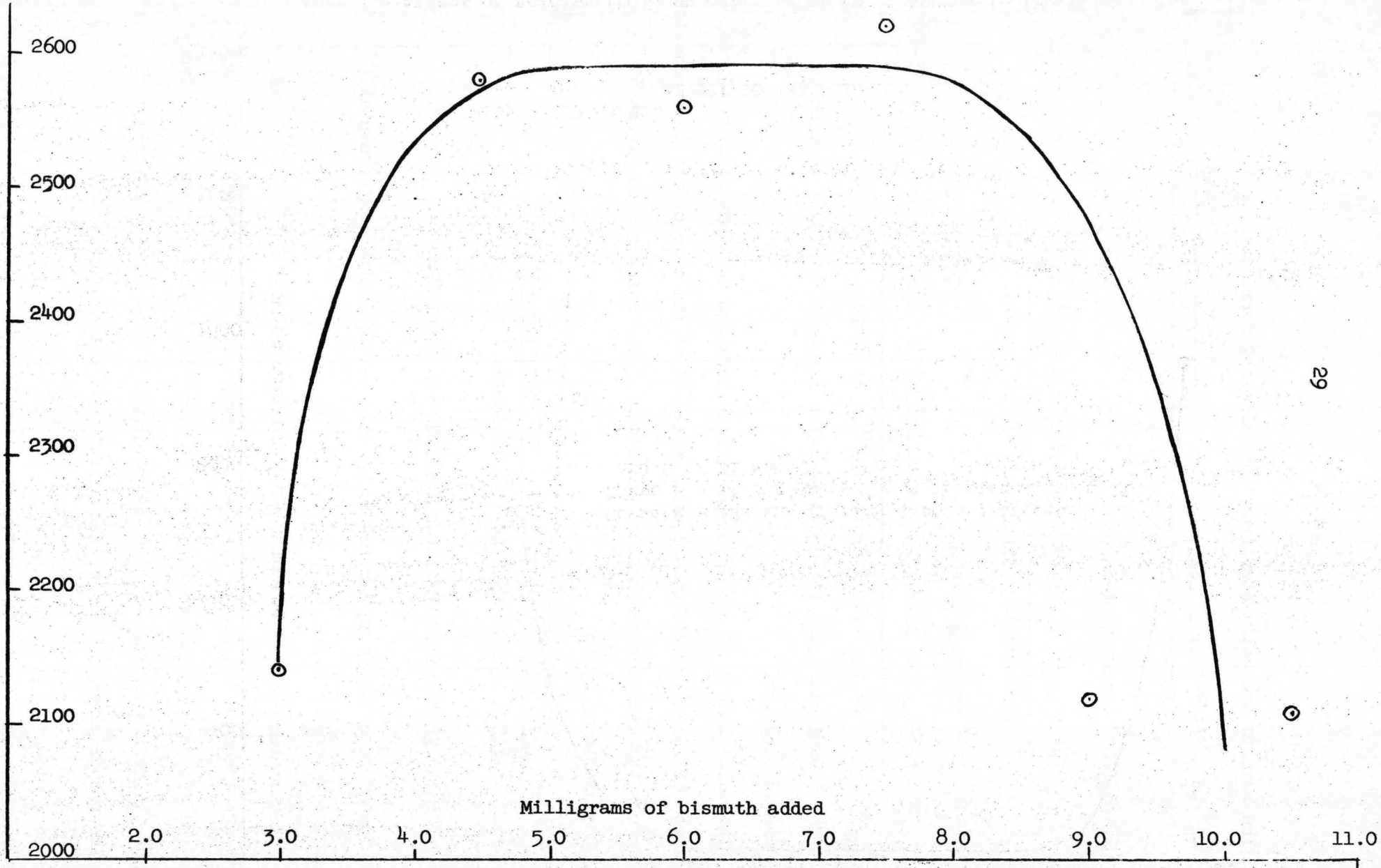

Figure 6.--Optimum amount of bismuth carrier required for Po^{210} precipitate

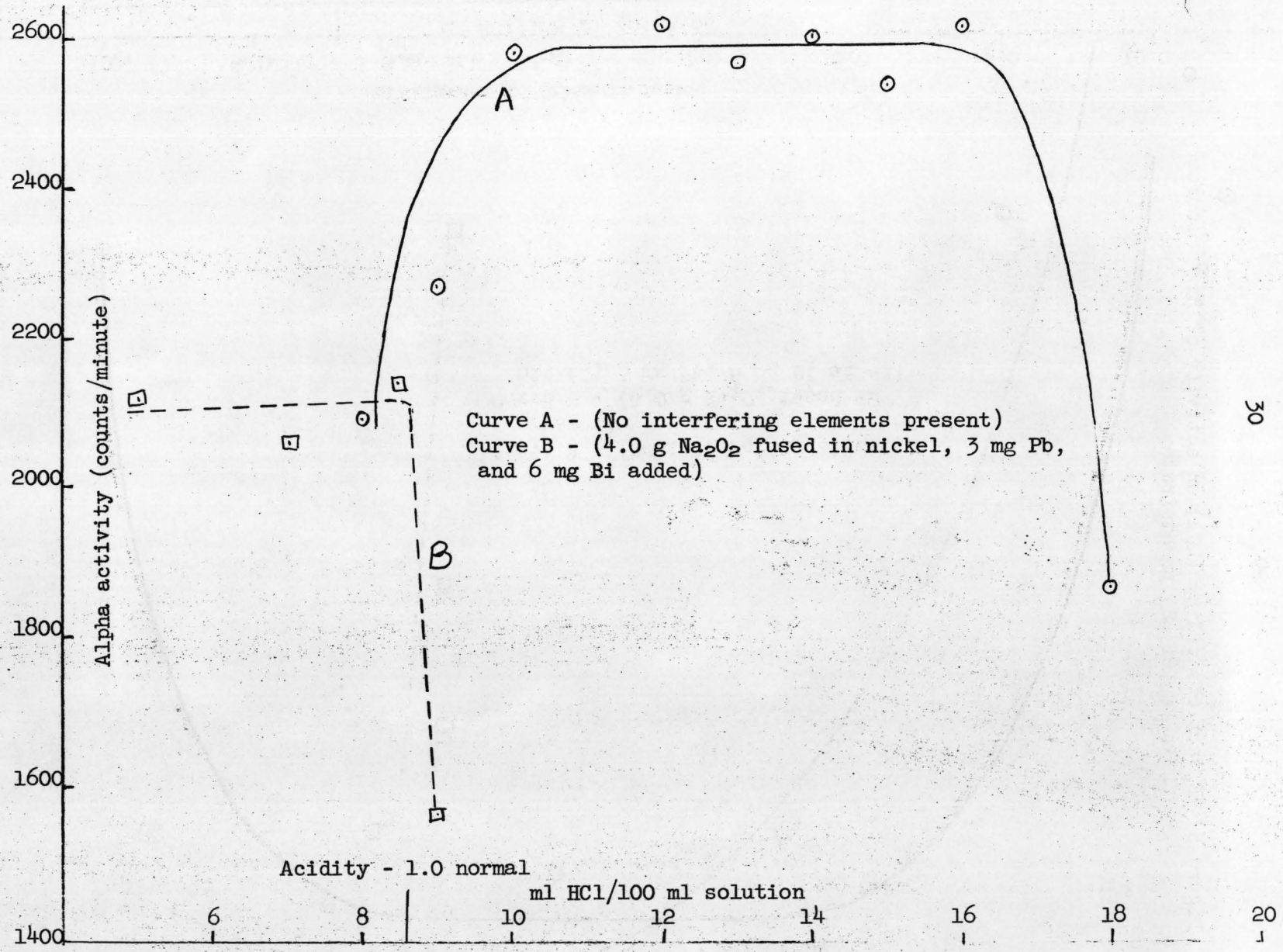

Figure 7.--Effect of acidity (HCl) on activity of Po^{210} source in $(Po,Bi)_2S_3$ precipitate

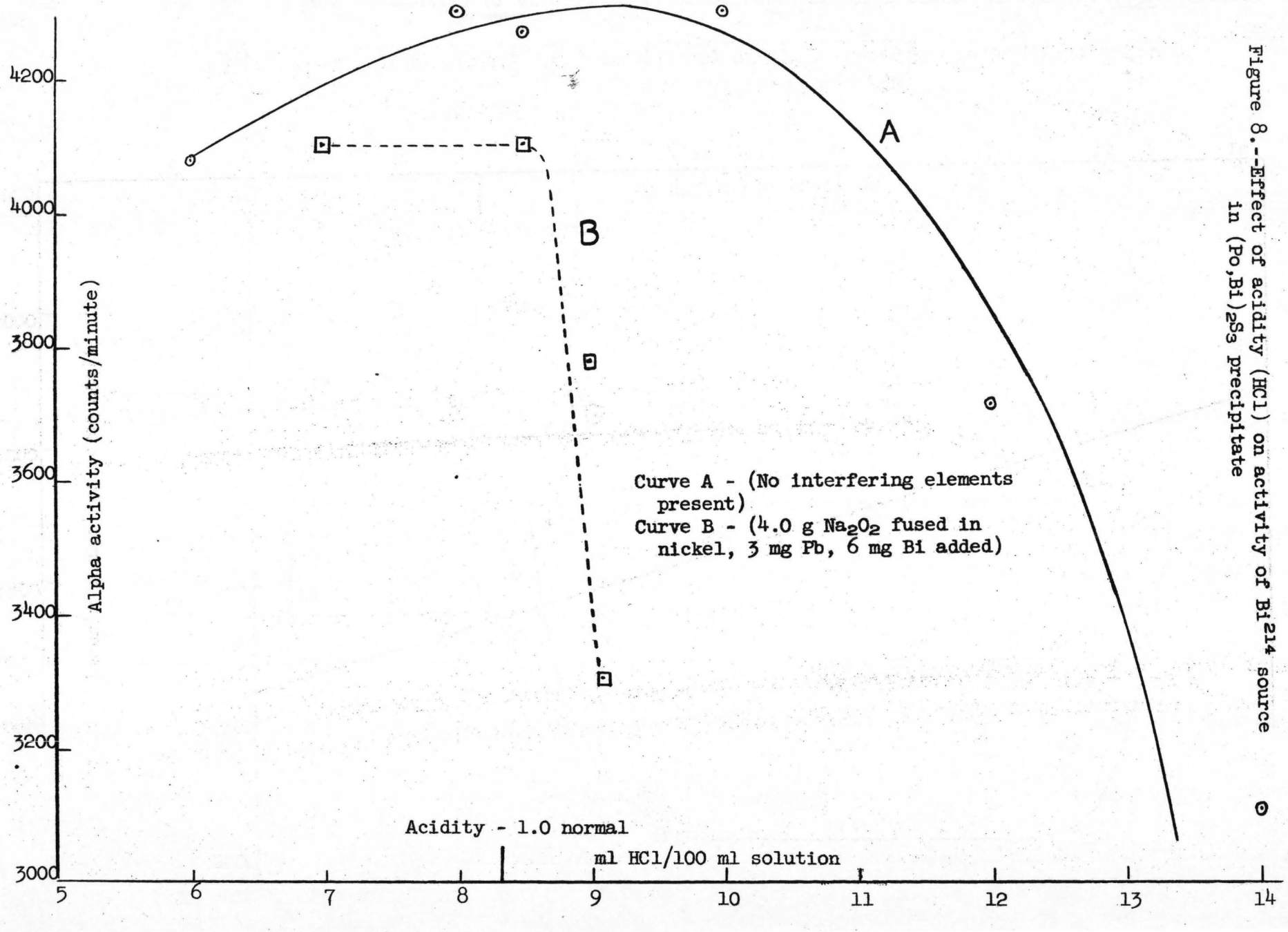

Figure 8.--Effect of acidity (HCl) on activity of Bi^{214} source in $(Po,Bi)_2S_3$ precipitate

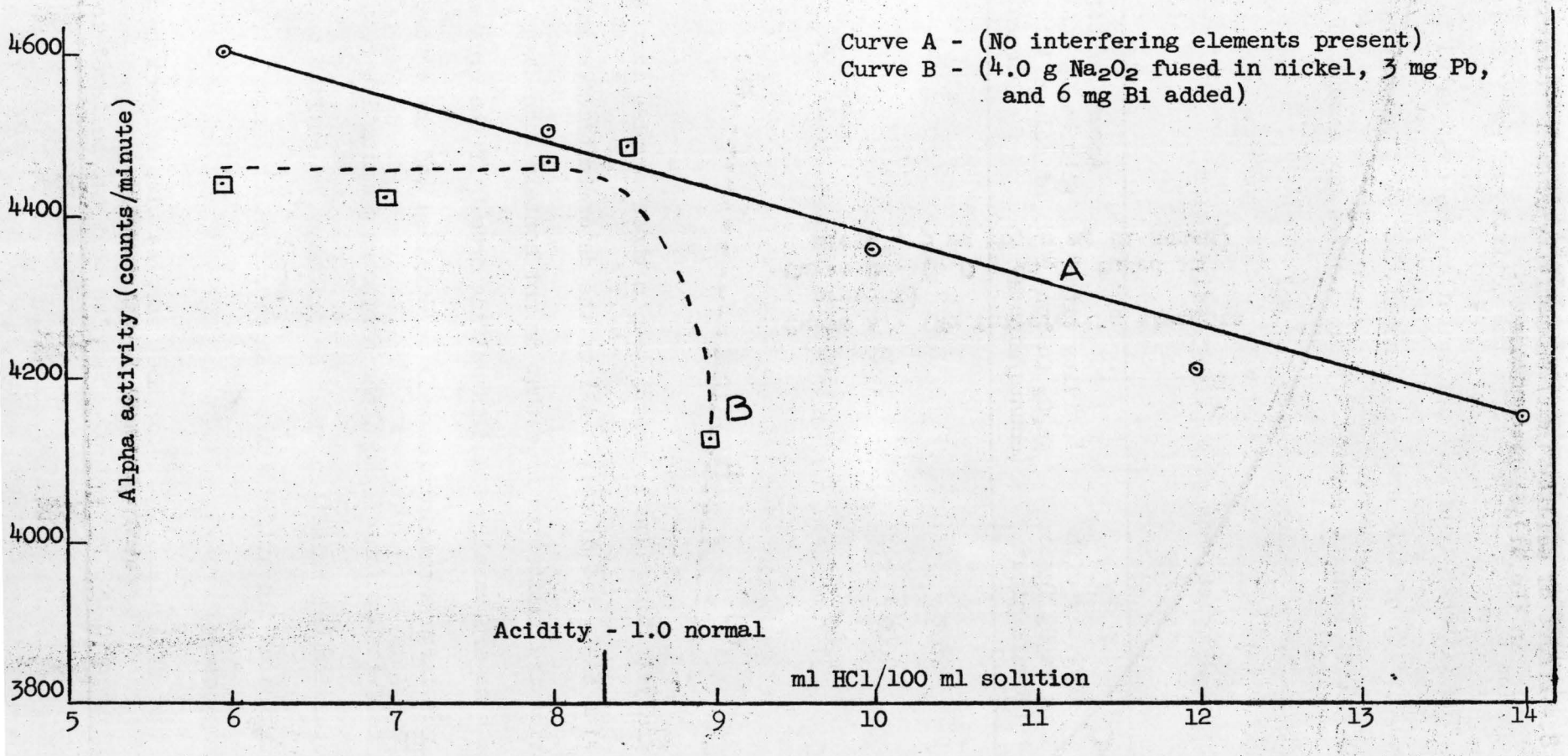

Figure 9.--Effect of acidity (HCl) on activity of Bi^{212} source in $(Po,Bi)_2S_3$ precipitate

A sulfide precipitate from a standard Po^{210} source without a sodium peroxide fusion was used to determine the activity of Po^{210} in column 2 of table 6. The filtrate from this precipitation was evaporated to dryness. The alpha activity of this evaporate showed that 99.7 percent of the Po^{210} is precipitated with bismuth sulfide. Table 6 shows the amount of each isotope precipitated after a sodium peroxide fusion.

Table 6.--Completeness of sulfide precipitation

1 Isotope	2 Activity with no Na_2O_2 fusion (counts/minute)	3 Activity with Na_2O_2 fusion (counts/minute)	Amount precipitated with Na_2O_2 fusion (ratio of column 3 to column 2) (percent)
Po^{210}	2590	2110	82
Bi^{212}	4600	4460	97
Bi^{214}	4280	4100	96

LIMITATIONS

The analysis for radon is restricted to those samples that will go into solution with Na_2O_2 immediately. All of the determinations using sulfide precipitation are limited to ores that do not contain such large amounts of heavy metals as are usually found in sulfide ores. If the ores are heavy sulfides, too large a precipitate will be obtained and the effect will be excessive self-absorption of the alpha particles causing low results. However, the thorium determination could be performed on sulfide ores by a reprecipitation of the sulfides after an overnight or longer wait for the Bi^{212} to regenerate.

The lower analytical limit for most samples with respect to total activity is about 0.020 percent eU. Samples that are believed to contain only

thorium can be analyzed at a slightly lower eU. In analyzing for a combination of radon^{222} and thorium the lower analytical limit, for the same degree of accuracy, may be slightly higher than the 0.020 percent eU mentioned above. For samples containing approximately 1 percent uranium or thorium, the error in reproducibility of results is about 5 percent for radon^{222} and thorium^{232} and about 8 percent for Pb^{210}. Radium content of less than 10^{-12} curies/g sample can be determined with the emanation method.

In the presence of high thorium^{232} content with respect to radon^{222}, the radium^{226} analysis can usually be used for radon in calculating the equivalent uranium for purposes of checking.

DISCUSSION

The fact that a uranium-bearing ore is or is not in equilibrium with its decay products is of prime importance to the geochemist. In order to make a radiometric assay of the ore, equilibrium is a prerequisite. For a large number of problems it is necessary to have a quantitative measure of the amount of disequilibrium especially for radium, radon, and lead. For instance, in any radioactive age method it is necessary to know the state of equilibrium of a given sample. For these and a host of other problems the foregoing method can prove to be a useful tool in determining the degree of equilibrium within a sample.

The following possibilities of uranium-thorium^{230}-radium^{226} disequilibrium indicate some probable reasons for the cause of disequilibrium. Underlined causes should be the most probable. The symbol = means "in equilibrium."

Case 1. $(U = Th^{230}) > Ra^{226}$: indicates Ra leach or U + Th deposition. If $Pb^{210} > Ra^{226}$, this indicates greater probability of very recent (within 100 years) Ra leach only.1/

Case 2. $(U = Th^{230}) < Ra^{226}$: indicates Ra deposition, or U + Th leach. If $Pb^{210} < Ra^{226}$, this indicates greater probability of recent Ra deposition only.

Case 3. $U > (Th^{230} = Ra^{226})$: indicates recent U deposition or recent Th + Ra leach.

If $Pb^{210} > Ra^{226}$, this indicates greater probability of Th + Ra leach only.

Case 4. $U < (Th^{230} = Ra^{226})$: indicates U leach or Th + Ra deposition or old Th deposition. If $Pb^{210} < Ra^{226}$, this indicates greater probability of recent Th + Ra deposition.

Case 5. $U > Th^{230} > Ra^{226}$: indicates relatively young sample.

Case 6. $U > Th^{230} < Ra^{226}$: indicates recent Th leach or Ra deposit on young sample. If $Pb^{210} < Ra^{226}$, this indicates greater probability of Ra deposit.

Case 7. $U < Th^{230} > Ra^{226}$: indicates Th deposit or U leach of young sample.

Case 8. $U < Th^{230} < Ra^{226}$: indicates differential deposition of Ra and Th, or differential leaching of U + Th. If $Pb^{210} < Ra^{226}$, this indicates greater probability of differential deposition of Ra and Th.

1/ $Pb^{210} < Ra^{226}$ can be used only where $Rn^{222} = Ra^{226}$ because of the possibility of Pb^{210} loss with long-continued Rn emanation.