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**RADIUM-BARIUM SEPARATION PROCESS
II - CHROMATE FRACTIONATION PROCEDURES**

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ABSTRACT

A comprehensive study was made of various fractionation systems for the fractional separation of barium-radium mixtures. The most efficient and simplest fractionation scheme was chosen on the basis of the thermodynamics of separating the constituents of mixed crystals and of combining fractions in a system of repeating composition. This scheme was applied to the separation of barium and radium by utilizing the countercurrent batch fractionation of the chromates. The chromate procedure was evaluated by a comparison with the classic methods which employ the fractional crystallization of the halides. The chromate method is more practical on the basis of radium enrichment per fractionation step, control of precipitating conditions, simplicity, and speed of operation.

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INTRODUCTION

Radium and barium are difficult to separate because of their chemical similarity and because all known salts of the two elements are isomorphous; hence, fractional methods (fractional crystallization or fractional precipitation) are required for their separation. The methods depend on the fact that precipitation or crystallization of a specific fraction of barium salt will carry (coprecipitate) from solution some different fraction of the radium salt. Radium was first separated from barium by fractional crystallization. Today, more than 50 years since its discovery, radium is still obtained primarily by the laborious, time- and space-consuming fractional crystallization of its halides.^{1,2,3,4,5,6,7} When a barium and radium bromide mixture (Ba:Ra = 400,000:1) is subjected to fractional crystallization, at least 23 fractionations⁸ are necessary before the crystals in the head fraction show a Ba:Ra ratio of 1:9.

Various methods utilizing sulfates,⁹ chromates,^{10,11} hydroxides,³ carbonates,^{12,13} and nitrates,¹⁴ have been suggested for the separation of barium and radium by fractional precipitation. None of the methods could compete with fractional crystallization. However, a radium enrichment equivalent to 23 fractional crystallizations may be obtained in only 8 to 12 fractional chromate precipitations, if the procedure given in this report is used. It must be emphasized that fewer fractionation steps in a radium recovery process mean less operating cost, time, equipment, and space, and a smaller retention of radium in intermediate fractions.

The chromate procedure presented in this report is a repeated fractional precipitation scheme and is operated in a countercurrent batch manner. Solid and liquid fractions of the same Ba:Ra ratio are combined, and original material (feed) is added at regular intervals. The fraction of barium precipitated in each fractionation step depends on the quantity of chromate ion added to the reaction mixture. The barium-radium chromate fraction is precipitated at each step by neutralizing a dilute nitric acid solution. The acid is neutralized as a result of the hydrolysis of internal reactants, such as urea or an alkali cyanate. Essentially, ammonia is added internally and homogeneously throughout the solution, thus eliminating localized precipitations which occur when reagents are added from an external source. The chromates precipitated in this manner are very granular and are filtered easily.

Since the chromate ion concentration of the solution is used to determine the fraction of barium precipitated, chromate ion in excess of the desired amount must be removed prior to making the precipitation. This situation occurs in the reprecipitation of the chromate precipitates which are richer in radium than the feed. It has been found that the chromate precipitate may be converted to a nitrate by extraction with hot concentrated nitric acid in which the barium-radium nitrate is not soluble. After dissolving the nitrate in water, controlled amounts of nitric acid and chromate may be added. In addition to providing simple and accurate control of the subsequent precipitation, the nitric acid extraction, by removing the highly radioactive daughters of radium, reduces the shielding requirements and the potential health hazard, and by extracting metals whose nitrates are soluble in concentrated nitric acid, serves as a purification step. Lead, however, is not removed.¹⁵

The following report also includes supporting data which were necessary to select the procedure that provided the best combination of simplicity and efficiency. A theory based on systems with repeating fractions was devised and applied to the fractionation of the chromates.

Because of its present industrial importance, fractional crystallization of the halides was taken as the basis of comparison for any new fractionation system of barium-radium mixtures. The comparison is made in the latter part of the report.

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SECTION I
COMPARISON OF VARIOUS FRACTIONATION SYSTEMS

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The distribution studies discussed in the previous report¹⁸ indicate that radium could be more rapidly separated from barium by fractional chromate precipitation than by the fractionation of any other barium-radium salt. Three factors, yield, enrichment, and simplicity, seem to be of primary importance in determining the efficiency of a fractionation system. A proper choice of fractionation system is necessary if the separation is to be efficient enough to compete with existing fractional crystallization systems. The desired system would be the simplest scheme in which the highest possible enrichment is obtained with the least possible decrease in yield. In this section several workable systems are compared, and the most satisfactory one was chosen for the separation of barium and radium by fractional chromate precipitation.

THEORY OF SYSTEMS WITH REPEATING FRACTIONS

A typical triangular fractionation scheme is shown in Figure 1. Individual fractions are represented by the circles. The fractions are designated by a row number and a column letter. Consider the separation of two components, *A* and *B*, by fractional crystallization or fractional precipitation. If a constant fraction *x* of Component *A* is precipitated at each operation and fractions are combined in the usual triangular fractionation scheme, the fraction of the original *A* which will appear at any point in the scheme is given by the terms of the binomial expansion of $[x + (1 - x)]^n$ as shown in Figure 1. In similar fashion for Component *B*, where a different but constant fraction *y* is precipitated at each step, the distribution of *B* in the various fractions will be given by the expansion of $[y + (1 - y)]^n$.

Fractionation schemes are simplified when fractions of repeating composition recur at regular intervals. The first fraction which can have the same composition as the original mixture is Fraction 2b. In this case every fraction will have the same composition as the fraction vertically above it in the scheme. The composition of Fraction 2b will be the same as the original if the fraction of *A* which reaches that point in the scheme is the same as the fraction of *B* which also reaches that point; i.e., $2x(1 - x) = 2y(1 - y)$. This equation is satisfied by two solutions

$$x = y,$$

$$\text{and } x = 1 - y.$$

The first solution, $x = y$, is a trivial solution. Although the concentrations of the fractions in the same vertical columns are the same, the end fractions also have the same composition, and no separation of the two components results. Therefore, $x = y$ is the equation for the line of no-separation. This equation is plotted in Figure 2. The line $x = y$ divides the diagram into two sections. Points above the line of no-separation represent enrichment of Component *B* in the precipitate. (The enrichment,¹⁸ expressed by the ratio of *y* to *x*, is greater than 1.0 for any points in this region.) Below the line, depletion of *B*, or enrichment of *A*, occurs in the precipitates.

The second solution, $x + y = 1$, is the one of interest since it gives repeating compositions for fractions in the same vertical columns and at the same time gives enrichment in the end fractions (column a, Figure 1) of $(y/x)^n$. This equation, also plotted in Figure 2, might be termed the operating line for a repeating composition in Fraction 2b.

The next fraction in the triangular scheme which can repeat the original composition is Fraction 3b. This fraction will be the same as the original providing

$$x^2(1 - x) = y^2(1 - y)$$

TRIANGULAR FRACTIONATION SCHEME

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OPERATING CURVES AND POINTS FOR
SYSTEMS WITH REPEATING COMPOSITION

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one solution of which is again $x = y$. Dividing by $y - x$ reduces the equation to

$$y^2 - (1 - x)y - (1 - x)x = 0,$$

a quadratic in y . This equation has two solutions

$$y = \frac{(1 - x) \pm \sqrt{(1 - x)^2 + 4(1 - x)x}}{2}.$$

The negative solution has no physical meaning since negative fractions of a component cannot be precipitated. The positive solution, plotted in Figure 2, is the operating line for a repeating composition in Fraction 3b. An operating line for Fraction 3c also can be plotted since a complementary relationship holds between the points on Curves 3b and 3c. For a point x, y on Curve 3b, the corresponding point on Curve 3c will be $(1 - x), (1 - y)$.

Fraction 4b will have the same composition as the original if $x^3(1 - x) = y^3(1 - y)$. Values which satisfy this fourth degree equation were obtained by a method of trigonometric substitution. From these values an operating line for a repeating composition in Fraction 4b was plotted in Figure 2. In a similar manner, operating lines were obtained for repeating compositions in Fractions 5b and 5c. Operating lines for Fractions 4d, 5d, and 5e also can be plotted since a complementary relationship exists between the points on Curves 4b and 4d, 5b and 5e, and 5c and 5d. The trigonometric substitution method and the solutions for the equations of the operating lines are given in Appendix A.

The operating lines plotted in Figure 2 are perfectly general for the fractionation of any pair of salts in which a constant fraction of each salt can be precipitated or crystallized. They represent all possible combinations of x and y which repeat the original composition within the first five rows of fractions. Repeating compositions in fractions beyond the fifth row ($n > 5$) are not considered since in practice such systems become too complicated. The relative amounts of the two salts which will precipitate in any specific case is a function of the relative solubilities of the two salts, their isomorphous properties, and the fractionation conditions.

In the chloride fractional crystallization of radium and barium mixtures, approximately 50 per cent of the barium and 80 per cent of the radium is crystallized at each crystallization step.⁴ These values plotted in Figure 2, letting x equal the fraction of barium and y the fraction of radium crystallized, give the point (0.5, 0.8). This point falls close to the operating curve for a repeating composition in Fraction 3b, which is the fraction to which original material is added in chloride crystallization systems in actual practice.

When barium-radium bromide mixtures are fractionally crystallized, 33.3 per cent of the barium will carry 83.1 per cent of the radium at each crystallization step.² The point in Figure 2 obtained from these values falls on the operating curve for Fraction 5c. In actual practice, original material is added to this fraction.

For a number of salts (including the barium-radium chromate mixtures discussed in the previous report¹⁸) the relationship between the amounts of the two components precipitated follows fairly closely the logarithmic equations proposed by Doerner and Hoskins,⁹

$$\frac{\log(\text{fraction of radium left in solution})}{\log(\text{fraction of barium left in solution})} = \lambda.$$

Using the notation given in Figure 2,

$$\frac{\log (1-y)}{\log (1-x)} = \lambda,$$

where x and y equal the fraction of barium and radium precipitated, respectively. The value of the constant, λ , depends on the precipitation conditions. For the purpose of illustration a value of 7.213 was chosen for λ , which approximates the value obtained for the fractional chromate precipitations at 0°C. This Doerner and Hoskins Curve is plotted in Figure 2. The intersections of this curve with the operating curves are operating points for fractionation systems having fractions of regularly repeating composition. Schemes having repeating fractions could be built up by precipitating the various percentages of Component A in accordance with Table I.

TABLE I
OPERATING DATA FOR VARIOUS FRACTIONATION SCHEMES

REPEATING FRACTION	PER CENT OF A PRECIPITATED* ($x \cdot 100$)	YIELD OF B PRECIP- ITATED IN PER CENT* ($y \cdot 100$)	ENRICHMENT OF B PER FRACTIONATION STEP (y/x)
5e	6.9	40.2	5.84
4d	8.8	48.4	5.55
3c	12.2	60.5	4.96
5d	15.1	69.1	4.58
2b	20.0	80.0	4.00
5c	25.9	88.3	3.41
3b	30.2	92.6	3.06
4b	37.2	96.3	2.59
5b	42.5	97.9	2.30

* VALUES DETERMINED GRAPHICALLY FROM FIGURE 2

The enrichment of Component B for a single precipitation is equal to y/x and is greatest for small values of x (Figure 3) reaching a maximum value of λ as x approaches zero (Appendix A). If it is desired to obtain B in high purity in a few steps, one would use an operating point on the lower part of the Doerner and Hoskins curve in Figure 2. Under these conditions the recovery of pure B, equal to y , is comparatively low. By operating at points higher on the distribution curve, higher yields are obtained but at a somewhat lower enrichment. In the separation of any large quantity of material this may be a more desirable condition. However, the maximum efficiency of separation will occur at some intermediate point which can be determined from a thermodynamic consideration based on the entropy change on separating the two components.

VARIATION OF ENRICHMENT WITH THE FRACTION
PRECIPITATED FOR A SYSTEM SHOWING
LOGARITHMIC DISTRIBUTION

ENTROPY OF SEPARATION

The entropy of mixing is given by the equation¹⁷:

$$\Delta S_{\text{mix}} = - \sum N_i R \ln x_i \quad (1)$$

where N_i and x_i are the number of moles and the mole fractions, respectively, of each component of the mixture. The entropy change on separating a mixture into its components would then be,

$$\Delta S_{\text{sepn.}} = -\Delta S_{\text{mix.}} = \sum N_i R \ln x_i \quad (2)$$

This equation is valid for ideal solutions. Mixtures of barium and radium salts may be considered as nearly ideal solid solutions, since the elements are isomorphous, almost identical in chemical behavior, and, since radium is usually present in the mixture only as a microcomponent.

The entropy of separation (ΔS) per mole of a binary mixture compared to the pure components can be calculated from the equation,

$$\Delta S = X_A R \ln X_A + X_B R \ln X_B \quad (3)$$

where X_A is the mole fraction of Component A, X_B is the mole fraction of Component B, and R is the gas constant. If the ratio $A:B > 100:1$, the first term of Equation 3 is less than one per cent of the total entropy change and the equation can be simplified,

$$\Delta S = X_B R \ln X_B \quad (4)$$

Since

$$X_B = \frac{B}{A+B}$$

where A equals the moles of Component A, and B equals the moles of Component B, then per mole of mixture,

$$\Delta S = \frac{B}{A+B} R \ln \frac{B}{A+B}$$

or, for $A+B$ moles of mixture,

$$\Delta S = \left(\frac{B}{A+B} R \ln \frac{B}{A+B} \right) (A+B)$$

which reduces to,

$$\Delta S = B R \ln \frac{B}{A+B} \quad (5)$$

For $A:B > 100:1$, $A+B \simeq A$, and

$$\Delta S = B R \ln \frac{B}{A} \quad (6)$$

or,

$$\Delta S = 2.303 R B \log \frac{B}{A} \quad (7)$$

With a general equation (Equation 7) for expressing the entropy of any mixture of A and B relative to pure A and B in which $A:B > 100:1$, it is possible to calculate the change in entropy on carrying out any given separation. If it is assumed that the original material is split into two fractions,

$$\Delta S = \Delta S_0 - \Delta S_1 - \Delta S_2 \quad (8)$$

in which, ΔS is the over-all entropy change, ΔS_0 is the entropy of the starting material relative to pure A and B , and ΔS_1 , and ΔS_2 , the entropies of Fractions 1 and 2 relative to pure A and B . From Equations 7 and 8,

$$\Delta S = 2.303 R \left[B_0 \log \frac{B_0}{A_0} - B_1 \log \frac{B_1}{A_1} - B_2 \log \frac{B_2}{A_2} \right] \quad (9)$$

in which, A_0 , A_1 , and A_2 equal the moles of Component A in the original mixture, Fraction 1, and Fraction 2, respectively, and B_0 , B_1 , and B_2 , the moles of Component B in the original mixture, Fraction 1, and Fraction 2. Since,

$$A_0 = A_1 + A_2 \quad (10)$$

and,

$$B_0 = B_1 + B_2 \quad (11)$$

$$\Delta S = 2.303 R \left[(B_1 + B_2) \log \frac{B_0}{A_0} - B_1 \log \frac{B_1}{A_1} - B_2 \log \frac{B_2}{A_2} \right]$$

which reduces to

$$\Delta S = -2.303 R \left[B_1 \log \frac{B_1/B_0}{A_1/A_0} + B_2 \log \frac{B_2/B_0}{A_2/A_0} \right] \quad (12)$$

If the entropy change is expressed in terms of the moles of B in the original mixture,

$$\Delta S = -2.303 R \left[\frac{B_1}{B_0} \log \frac{B_1/B_0}{A_1/A_0} + \frac{B_2}{B_0} \log \frac{B_2/B_0}{A_2/A_0} \right] \quad (13)$$

per mole of B_0 . For any fractional precipitation system, let the fraction of Components A and B precipitated be represented by x and y , respectively, and the fraction remaining in the solution by $1 - x$ and $1 - y$, that is,

$$x = \frac{A_1}{A_0}; \quad y = \frac{B_1}{B_0}; \quad 1 - x = \frac{A_2}{A_0}; \quad 1 - y = \frac{B_2}{B_0}$$

then,

$$\Delta S = -2.303 R \left[y \log \frac{y}{x} + (1 - y) \log \frac{1 - y}{1 - x} \right] \quad (14)$$

The decrease in over-all entropy indicates the amount of separation which is achieved. A maximum entropy change is obtained when the mixture is separated into two fractions, one of pure A and one of pure B. If no separation is attained in either fraction, the change in entropy will equal zero. Equation 14 also shows a relationship between the entropy change on separation and the concepts of yield and enrichment since the term, $y \log y/x$, represents yield multiplied by logarithm of the enrichment (or depletion) of Component B in the precipitate, whereas $(1 - y) \log (1 - y)/(1 - x)$ has a similar significance for the solution. For any separation the terms will always be opposite in sign, positive for enrichment of Component B in the fraction, but negative for depletion.

In order to apply Equation 14 to fractional precipitation, it is necessary to have an equation relating the relative amounts of A and B in the two fractions with respect to the starting mixture. For this purpose it will be assumed that an equation of the Doerner and Hoskins type is valid,

$$\log (1 - y) = \lambda \log (1 - x) \quad (15)$$

in which λ is the logarithmic distribution coefficient. Thus,

$$(1 - y) = (1 - x)^\lambda \quad (16)$$

and,

$$y = 1 - (1 - x)^\lambda \quad (17)$$

Substitution of these terms into Equation 14 gives,

$$\Delta S = -2.303 R \left\{ \left[1 - (1 - x)^\lambda \right] \log \left[\frac{1 - (1 - x)^\lambda}{x} \right] + (1 - x)^\lambda \log (1 - x)^{\lambda-1} \right\} \quad (18)$$

By differentiating Equation 18 with respect to $(1 - x)$ and equating the differential to zero,

$$-\frac{1}{2.303R} \cdot \frac{d\Delta S}{d(1-x)} = \frac{1 - (1-x)^\lambda}{x} + (1-x)^{\lambda-1} \left\{ \left[2.303 \lambda \log \frac{x(1-x)^{\lambda-1}}{1 - (1-x)^\lambda} \right] - 1 \right\} = 0 \quad (19)$$

values of $(1 - x)$ which yield maximum entropy changes at various values of λ may be determined. Several solutions of Equation 19 are listed in Table II from which corresponding values for x and y were calculated.

When these x and y values were plotted in Figure 4, a curve was obtained which represents points of maximum entropy change ($\Delta S_{\max}$) between λ values of 1.01 and 1.024. For any system having an intermediate value of λ the point of maximum entropy change is determined by the intersection of this curve with the Doerner and Hoskins curve for the system. For example, as indicated in Figure 4, the maximum entropy change for a fractionation system having a λ value of 7.213 will occur when x and y have values of 0.273 and 0.900, respectively.

Equation 18 is used to calculate the entropy change (ΔS) for any fractionation system for which are known the logarithmic distribution coefficient (λ) and the fraction $(1 - x)$

MAXIMUM ENTROPY OF SEPARATION

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of Component A left in solution. The maximum entropy change ($\Delta S_{\max}$) for any particular value of λ may also be calculated by substituting into Equation 18 the value of $(1 - x)$ obtained either graphically or from Equation 19. An evaluation of yield and enrichment for a given fractionation system can be made by comparing its ΔS value with the $\Delta S_{\max}$ calculated for the same value of λ .

TABLE II

POINTS OF MAXIMUM ENTROPY CHANGE FOR VARIOUS VALUES OF λ

λ	$(1 - x)$	x	y
1.01	0.191	0.809	0.8121
2	0.398	0.602	0.842
4	0.592	0.408	0.877
8	0.747	0.253	0.9030
16	0.852	0.148	0.9229
64	0.955	0.045	0.9475
128	0.9761	0.0239	0.9548
256	0.9873	0.0127	0.9621
1,024	0.9966	0.0034	0.9695

CHOICE OF PROPER REPEATING FRACTION

The maximum change in entropy for a fractionation scheme which has a λ value of 7.213 occurs when the fraction of Component A precipitated (x) equals 0.273 and the fraction remaining in solution $(1 - x)$ equals 0.727. Substitution of these values into Equation 18 yields a maximum value for $-\Delta S/2.303R$ of 0.3799 entropy units. The value for x of 0.273 does not correspond to that for any of the fractionation schemes listed in Table I. Some efficiency of separation must therefore be sacrificed to obtain repeating fractions.

In Table III are listed the $-\Delta S/2.303R$ values for the various fractionation schemes of Table I. These were calculated from Equation 18 by substitution of their respective values for x and $(1 - x)$. The per cent of maximum entropy change ($\Delta S/\Delta S_{\max} \times 100$) for each fractionation scheme was calculated, and these are also listed in Table III.

The entropy of separation values may be used to select a fractionation scheme for the fractionation of Components A and B. It is again assumed that the logarithmic distribution coefficient equals 7.213. On this basis, fractionation schemes in which Fractions 5c and 3b are the repeating fractions are the best since they yield ΔS values which are more than 99 per cent of $\Delta S_{\max}$. However, as will be shown, the scheme in which Fraction 2b repeats the composition of the original mixture must be considered because of its simplicity. If Fraction 2b is the repeating fraction, there is a slight loss in efficiency of separation since ΔS is only 95.1 per cent of $\Delta S_{\max}$. All other schemes may now be eliminated because of their lower entropies of separation.

TABLE III
COMPARISON OF THE ENTROPIES OF SEPARATION FOR VARIOUS
FRACTIONATION SCHEMES

REPEATING FRACTION	$\frac{-\Delta S}{2.303R}$	$\left(\frac{\Delta S}{\Delta S_{MAX}} \times 100 \right)$
5e	0.1932	50.9
4d	0.2321	61.1
3c	0.2876	75.7
5d	0.3230	85.0
2b	0.3613	95.1
5c	0.3792	99.8
3b	0.3773	99.3
4b	0.3558	93.7
5b	0.3289	86.6

Fractionation schemes in which 2b, 3b, and 5c are repeating fractions are shown in Figure 5. It is assumed that the stipulations of the fractionation of A and B require that one end product (e.g., precipitates) has at least a 1,000-fold enrichment of Component A whereas the other end product (filtrates) shows at least a 100-fold depletion. The individual fractions in Figure 5 are represented by the circles; those which are repeating fractions by solid circles.

The simplest fractionation scheme would require the fewest number of fractions (hold-up fractions) between successive additions of starting mixture. For the fractionation schemes shown in Figure 5, only 8 hold-up fractions are necessary if 2b is the repeating fraction compared to 15 and 20 hold-up fractions, respectively, if 3b and 5c are the repeating fractions. Therefore, fewer individual operations would be required in the case of the former. When 2b repeats the composition of the original mixture, every fraction has the same composition as a fraction vertically above it in the scheme. It may be noted from Figure 5 that the same is not true when 3b and 5c are the repeating fractions.

CONCLUSION

The fractionation system based on the repetition of the original composition in Fraction 2b is the simplest scheme in which the highest possible enrichment is obtained with the least possible decrease in yield. Therefore, this system was applied to the fractionation of barium-radium mixtures.

COMPARISON OF THE SIMPLICITY OF FRACTIONATION SYSTEMS HAVING REPEATING COMPOSITIONS

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SECTION II

THE COUNTERCURRENT BATCH FRACTIONATION SCHEME

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The most satisfactory fractionation scheme for the separation of barium and radium has been chosen on the basis of simplicity, yield, and enrichment. The scheme involves repetition of the original composition in Fraction 2b (Section I). The necessary condition for repetition has been shown to be that the sum of the fractions (x and y) of each component precipitated is equal to one, i.e., $x + y = 1$.

A continuous fractionation scheme would be desirable for the processing of barium and radium since it would lead to less hold-up for radium. The proposed fractionation scheme is essentially a batch process but can be operated on a nearly continuous basis, if a constant amount of fresh feed solution is added to Fraction 2b each time it appears in the scheme. The amount of material in each fraction then builds up to some constant equilibrium value which determines the container size for that fraction. Equations have been developed for this batch countercurrent system to predict the amounts of the two constituents at equilibrium and the enrichment obtained for any number of fractionation steps.

The proposed fractionation scheme is outlined in Figure 6A for Component A. The flow of A in the solutions is indicated by the upper arrows and in the precipitates by the lower arrows. Feed of the starting mixture enters at the central Fraction 0 and removal of the final precipitate and solution after k fractionation steps is indicated at k and $-k$, respectively. For a material balance:

$$A_F = A_k + A_{-k} \quad (1)$$

where A_F is the amount of Component A added in the feed and A_k and A_{-k} are the amounts of A removed in the final precipitate and solution, respectively.

At each step the fraction x of Component A is precipitated and $1 - x$ is left in solution. Since $x + y = 1$, a complementary relation holds for Component B, i.e., the fraction $1 - x$ is precipitated and x remains in solution. The enrichment (E) of Component B occurring at each step is therefore $\frac{1-x}{x}$ and in k steps the enrichment (E_k) is $\left(\frac{1-x}{x}\right)^k$. The ratio of A in the final solution to A in the final precipitate is given by:

$$\frac{A_{-k}}{A_k} = \left(\frac{1-x}{x}\right)^k \quad (2)$$

The amount of A in Fraction 0 can be shown to be:

$$A_0 = \frac{A_{-k} - A_k}{1 - 2x} \quad (3)$$

Starting with Fraction 0, the general equation for the amount of Component A in Fraction n can be found as follows:

$$P_1 = A_0 x \text{ and } S_1 = A_0 (1 - x)$$

where P_1 and S_1 are the amounts of Component A in the precipitate and solution, respectively, as designated in Figure 6A. Similar equations hold for the precipitate and filtrate from Fraction 1:

$$P_2 = A_1 x \text{ and } S_2 = A_1 (1 - x)$$

From a material balance of the over-all cycle,

$$S_2 = P_1 - A_k = A_0 x - A_k$$

A-FRACTIONAL PRECIPITATION SCHEME, GENERAL CASE:

B-NUMERICAL EXAMPLE, SHOWING DISTRIBUTION OF BARIUM IN A 4 STEP FRACTIONATION WITH 20% OF THE BARIUM CARRYING 80% OF THE RADIUM.

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FIGURE 6

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A_1 in terms of A_0 can be obtained by combining the two equations for S_2 .

$$A_1 = \frac{A_0 x - A_k}{1 - x} \quad (4)$$

From this basic equation, A_2 in terms of A_0 is found to be:

$$A_2 = A_0 \left[\frac{x}{1-x} \right]^2 - \frac{A_k}{1-x} \left[\frac{x}{1-x} + 1 \right]$$

Letting $z = \frac{x}{1-x}$, and rearranging terms, the general equation for A_n in terms of A_0 is found to be:

$$A_n = A_0 z^n - \frac{A_k}{1-x} \left[1 + z + z^2 + \dots + z^{n-1} \right] \quad (5)$$

where

$$0 < n < k$$

For fractions to the right of the feed, a similar relationship holds;

$$A_n = \frac{A_0}{z^n} - \frac{A_k}{x} \left[1 + \frac{1}{z} + \frac{1}{z^2} + \dots + \frac{1}{z^{n-1}} \right] \quad (6)$$

Because of the reciprocal relationships between the enrichment of A and B , Equation 5 can be used to calculate the amounts of B in the fractions to the right of the feed and Equation 6 for the amounts of B to the left of the feed. The preceding equations, in general, apply only for an equal number of enrichment and depletion steps.

For the fractionation of mixtures where one component is present in relatively small amounts, as is the case with barium and radium, the total weight of each fraction can be taken to be that of the major component.

A numerical example for the separation scheme is given in Figure 6B, as it might be applied to the separation of barium and radium. It is assumed that 20 per cent of the barium is precipitated at each step and that it carries 80 per cent of the radium, $x = 0.20$ and $1 - x = 0.80$, and that four fractionations are carried out on the enrichment and depletion sides. The distribution of barium is shown (Figure 6B), assuming that one part of barium is removed at the radium-rich end, $A_k = 1$.

The enrichment per step is then $\frac{0.80}{0.20} = 4.0$ and for four steps $E_4 = \left(\frac{1-x}{x} \right)^4 = 256$ (also equals A_k). From Equation 1, the feed $A_F = 257$ and from Equation 3, $A_0 = 425$. Using Equations 5 and 6, the values for A_1 , A_2 , A_3 , and for A_{-1} , A_{-2} , and A_{-3} , were calculated in terms of $A_0 = 425$.

The reciprocal relationship for radium can be shown from the numerical example by assuming a feed containing 257 grams of barium and 257 micrograms of radium. The final precipitate recovered as A_4 would contain one gram of barium and 256 micrograms of radium, and the discard solution would contain 256 grams of barium and 1 microgram of radium. Expressed on a percentage basis, 99.61 per cent of the radium would be recovered in 0.39 per cent of the barium. The over-all enrichment factor of 256 would bring the Ba:Ra ratio from 1,000,000:1 down to 3,906:1 for the four steps considered.

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SECTION III
CONCENTRATION OF RADIUM BY THE
COUNTERCURRENT BATCH FRACTIONATION PROCESS

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The countercurrent batch fractionation scheme, described in the preceding section, was used in the following fractional precipitation studies for the separation of barium and radium. Barium and radium chromates were precipitated from homogeneous solution.¹⁸

The percentages of barium and radium which must be precipitated at each fractionation step if Fraction 2b repeats the composition of the original mixture were determined from Figure 7. These curves represent the percentages of the radium carried by the homogeneous precipitation of various percentages of the barium as barium chromate at 100°, 25°, and 0°C.¹⁸ (The dotted line is a typical Doerner and Hoskins curve for which $\lambda = 7.213$.) The intersections of the curves with the operating line for Fraction 2b are the operating points, i.e., the percentages of barium and radium which must be precipitated at each fractionation step. These percentages and the corresponding enrichment per fractionation step are tabulated in Table IV.

TABLE IV
OPERATING POINTS AND ENRICHMENTS FOR REPEATING
COMPOSITIONS IN FRACTION 2b

	PER CENT BARIUM PRECIPITATED	PER CENT RADIUM CARRIED	ENRICHMENT PER FRACTIONATION STEP*
CHROMATE METHOD AT 100°C	25	75	3.00
CHROMATE METHOD AT 25°C	22	78	3.55
CHROMATE METHOD AT 0°C	19	81	4.26
CALCULATED FOR $\lambda = 7.213$	20	80	4.00

* ENRICHMENT = $\frac{\text{PER CENT Ra}}{\text{PER CENT Ba}}$

For ease of manipulation the chromate procedure at 25°C was chosen in preference to the other two procedures. Each fractionation step requires the precipitation of 22 per cent of the barium and 78 per cent of the radium, and, thus, a radium enrichment of 3.55 is obtained.

The fractionation system used in these studies is a double withdrawal type¹⁸ as shown in Figure 8. The system is built up from starting samples of constant weight (A_0) by carrying out three fractionation steps on both the enrichment and depletion sides and by making repeated precipitations of 22 per cent of the total barium in each fractionation step. Fractions richer in radium than the original sample are represented by A with a positive subscript, whereas those poorer in radium are represented by A with a negative subscript. The system requires five additions of original material (feed) before the fractions are built up to constant weights. The constant weights at equilibrium can be calculated directly from equations given in Section II.

The barium distribution in the system based on a constant A_0 value of 100 is shown numerically in Figure 8. Feed is added to every A_0 fraction and radium-enriched and radium-impooverished materials are removed from the A_2 and A_{-2} fractions, respectively. Under equilibrium conditions the weight of material added to the system is equal to the sum of the weights of material removed.

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FIGURE 7

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FRACTIONATION OF RADIUM AND BARIUM BY
PARTIAL PRECIPITATION AS CHROMATES

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Arrows sloping to the right in Figure 8 indicate the flow of the filtrates in the system while the arrow sloping to the left indicate that of the precipitates. After the first appearance of each fraction in the scheme, a regular cycle of operations is established by which the various fractions are obtained as follows:

A_2 is the precipitate obtained from A_1 ;

A_1 is composed of precipitate from A_0 and filtrate from A_2 ;

A_0 is composed of the precipitate from A_1 , the filtrate from A_1 , and original material (feed);

A_1 is composed of the precipitate from A_2 and the filtrate from A_0 ;

A_2 is the filtrate obtained from A_1 .

PROCEDURE

The general procedure for the countercurrent batch fractional precipitation process follows. A more specific procedure for each fractionation step is given in Appendix B. Reagent data for building up the system are given in Table V. The procedure is essentially the same for each fraction although there are some modifications. Once the fractions attain constant weight the amounts of reagents used for individual fractionation steps do not change. The data in Table V are based on A_0 fractions of 100 grams of barium. For A_0 fractions of any other weight the amounts of reagents can be calculated from these tabulated values.

The starting solution for every fractionation step is 1.0 per cent in barium, 1.0 per cent in glacial acetic acid, and 0.06 normal in nitric acid. A weighed sample of potassium dichromate is added to the reaction mixture. Precipitation is effected by adding five grams of potassium cyanate for each liter of solution. The mixture is stirred during the precipitation which is complete within an hour after the addition of the cyanate. The final supernatant liquid is nearly colorless and has a pH of 5. The mixture is filtered, and the precipitate and filtrate are saved for subsequent fractionation steps.

The fraction of barium precipitated in each case is controlled by the amount of potassium dichromate added. It is to be stressed that, although the amount of chromate added at each step is sufficient to precipitate 20 per cent of the total barium, actually 22 per cent precipitates due to coprecipitation of barium nitrate. The acetic acid is added as a buffer to prevent the precipitation of barium carbonate.

Chromate precipitates which are equal to or poorer in radium than the original material are dissolved in nitric acid. This solution is used as part of the reaction mixture in the subsequent fractionation step. Since the amount of chromate ion present in the reaction mixture is insufficient to precipitate 20 per cent of the total barium, the addition of more potassium dichromate is required.

Chromate precipitates richer in radium than the original material are converted to nitrates by extraction with hot concentrated nitric acid. The resulting nitrates are dissolved in hot water and are used as part of the reaction mixture in the subsequent fractionation step. The extraction is necessary since the amount of chromate ion in each precipitate is more than enough to precipitate 20 per cent of the total barium. The proper quantity of potassium dichromate is then added to the reaction mixture.

TABLE V

REAGENT DATA FOR THE COUNTERCURRENT BATCH SYSTEM

RUN	REAGENTS	UNITS	A_2	A_1	A_0	A_1	A_2
1	Ba ⁺⁺	g.	4.840	22.00	100.0	78.00	60.84
	K ₂ Cr ₂ O ₇	g.	1.036	4.711	21.41	16.70	13.03
	HNO ₃	ml.	1.94	8.80	40.0	40.0	40.0
	HOAc	ml.	4.84	22.0	100		
	KCNO	g.	2.42	11.0	50	50	50
	TOTAL VOL.	ml.	484.	2,200.	10,000.	10,000.	10,000.
2	Ba ⁺⁺	g.	5.672	25.78	100.0	91.38	71.28
	K ₂ Cr ₂ O ₇	g.	1.214	5.520	4.711	6.539	15.26
	HNO ₃	ml.	2.27	10.3	47.3	45.7	40.0
	HOAc	ml.	5.67	25.8	100		
	KCNO	g.	2.84	12.9	50	50	50
	TOTAL VOL.	ml.	567.	2,580.	10,000.	10,000.	10,000.
3	Ba ⁺⁺	g.	5.812	26.42	100	93.68	73.07
	K ₂ Cr ₂ O ₇	g.	1.244	5.657	1.846	4.796	15.65
	HNO ₃	ml.	2.33	10.6	42.9	46.7	40.0
	HOAc	ml.	5.81	26.4	100		
	KCNO	g.	2.91	13.2	50	50	50
	TOTAL VOL.	ml.	581.	2,640.	10,000.	10,000.	10,000.
4	Ba ⁺⁺	g.	5.837	26.53	100.0	94.08	73.38
	K ₂ Cr ₂ O ₇	g.	1.250	5.681	1.353	4.499	15.71
	HNO ₃	ml.	2.34	10.6	42.1	46.9	40.0
	HOAc	ml.	5.84	26.5	100		
	KCNO	g.	2.92	13.3	50	50	50
	TOTAL VOL.	ml.	584.	2,650.	10,000.	10,000.	10,000.
5	Ba ⁺⁺	g.	5.841	26.55	100.0	94.14	73.43
	K ₂ Cr ₂ O ₇	g.	1.251	5.685	1.268	4.445	15.72
	HNO ₃	ml.	2.34	10.6	42.0	46.9	40.0
	HOAc	ml.	5.84	26.6	100		
	KCNO	g.	2.92	13.3	50	50	50
	TOTAL VOL.	ml.	584.	2,660.	10,000.	10,000.	10,000.

Barium chromate is converted to barium nitrate by passing hot concentrated nitric acid through a bed of the chromate on a sintered glass funnel. About 10 milliliters of acid per gram of barium chromate is used for the extraction and subsequent wash. The last traces of nitric acid and chromic acid retained on the barium nitrate crystals can be removed by washing with acetone. Essentially complete conversion of barium chromate to barium nitrate is accomplished by this method.

A suitable reagent for the extraction is commercial concentrated nitric acid, which is approximately 70 per cent nitric acid. The loss of barium in the nitric acid extract is small because of the low solubility of barium nitrate in concentrated nitric acid. Green¹⁹ reports the solubility of barium nitrate at 24.88°C as 197 milligrams per liter in 56.6 per cent nitric acid, 14.1 milligrams per liter in 71.15 per cent acid, and only 0.283 milligram per liter in 92.10 per cent acid. Willard and Goodspeed¹⁵ have devised a quantitative separation of barium from other alkaline earth metals which is based on the negligibly small solubility of barium nitrate in 76 per cent nitric acid.

The extractions are made with hot acid solutions since these yield more crystalline precipitates and more complete conversion to nitrate than do cold acid solutions. If desired, the chromate (as chromic acid) and the nitric acid in the extracts can be separated for reuse by distillation.

RESULTS AND DISCUSSION

Three series of experiments were carried out using the double withdrawal fractionation system described above and using three starting mixtures of widely differing barium-radium composition. In each case the fractions were built up to equilibrium weights before analysis of the radium-enriched and barium-enriched products. The products from the first series of experiments served as starting materials for the second and third series.

The Ba:Ra ratio of the original material for the first series of experiments was 102,300:1. This material was a purified barium-radium mixture obtained from uranium residues²². Fractions were built up from this starting material using A_0 fractions of 30 grams of barium which corresponds to an A_F of 17.6 grams of barium at equilibrium. The amounts of reagents required in each fractionation step were obtained by taking 30 per cent of the values listed in Table V. After equilibrium was established, the quantities of the various reagents used in each fractionation step remained constant. Approximately one kilogram of radiferous barium was processed by this procedure. Representative samples of both the radium-enriched and the barium-enriched products were analyzed for radium by the method of Thompkins and co-workers²⁰ and for barium by gravimetric methods. The results of these analyses are listed in Table VI for three typical experiments.

The average Ba:Ra ratio of the radium-enriched product was 2,530:1 and that for the barium-enriched product 3,016,000:1. The radium-enriched product contained on an average 93.9 per cent of the original quantity of radium and 2.3 per cent of the original quantity of barium as compared to the barium-enriched product which contained only 3.3 per cent of the original radium and 96.8 per cent of the original barium. The average radium enrichment factor for a single fractionation step was 3.43 which approximates the average enrichment factor of 3.55 previously reported¹⁶ for the chromate-cyanate method at 25°C.

TABLE VI
CONCENTRATION OF RADIUM BY THE COUNTERCURRENT BATCH PROCESS

	RUN	Ba (g.)	Ra (μ g.)	TOTAL Ba (%)	TOTAL Ra (%)	Ba:Ra RATIO
ORIGINAL		17.58	171.8	100.0	100.0	102,300:1
RADIUM-ENRICHED PRODUCT	6	0.3998	161.1	2.3	94.9	
	7	0.4127	160.6	2.3	93.5	
	8	0.4123	160.4	2.3	93.4	
	AV.	0.4083	161.4	2.3	93.9	2,530:1
BARIUM-ENRICHED PRODUCT	6	17.27	6.00	98.2	3.5	
	7	16.91	5.42	96.2	3.2	
	8	16.84	5.51	95.8	3.2	
	AV.	17.01	5.64	96.8	3.3	3,016,000:1

AVERAGE RADIUM ENRICHMENT FACTOR = 3.43

The original material used in the second series of experiments was composed of several samples which had an average Ba:Ra ratio of 2,695:1. Fractions of equilibrium weights were built up using A_0 fractions of one gram of barium. The weight of barium in each fraction was calculated by taking one per cent of the values given in Figure 8 and the amounts of reagents by taking one per cent of the values listed in Table V. Representative samples of both the radium-enriched product and the barium-enriched product were analyzed for radium and barium. The results for three typical experiments are listed in Table VII.

TABLE VII
CONCENTRATION OF THE RADIUM BY THE COUNTERCURRENT BATCH SYSTEM

	RUN	Ba (g.)	Ra (μ g.)	TOTAL Ba (%)	TOTAL Ra (%)	Ba:Ra RATIO
ORIGINAL	7	0.5858	218.2	"	"	"
	13	0.5858	209.5	"	"	"
	21	0.5858	224.3	"	"	"
	AV.	0.5858	217.3	100.0	100.0	2,695:1
RADIUM-ENRICHED PRODUCT	7	0.01285	206.6	2.2	94.7	
	13	0.01272	208.8	2.1	99.7	
	21	0.01267	202.2	2.2	90.1	
	AV.	0.01275	205.9	2.2	94.7	61.9:1
BARIUM-ENRICHED PRODUCT	7	0.5764	9.77	98.4	4.5	
	13	0.5763	7.48	98.4	3.6	
	21	0.5750	7.68	98.2	3.4	
	AV.	0.5759	8.31	98.3	3.8	69,032:1

AVERAGE RADIUM ENRICHMENT FACTOR = 3.52

The average Ba:Ra ratio of the radium-enriched product was 61.9:1 and that of the barium-enriched product 69,032:1. The radium-enriched product contained an average of 94.7 per cent of the original quantity of radium and 2.2 per cent of the original quantity of barium. The barium-enriched product contained 98.3 per cent of the original barium but only 3.8 per cent of the original radium, and the average radium enrichment factor for a single fractionation step was 3.52. This enrichment factor is slightly higher than the value reported in the first series of experiments.

In this second series of experiments a total of 4.270 milligrams of radium was processed. The system required 21 additions of feed (runs). A summation of the amounts of radium in the radium-rich and barium-rich products, and in the various fractions (A_2 , A_1 , A_0 , A_{-1} , and A_{-2}), residues, and acid distillates is tabulated in Table VIII. The radium-enriched products contained a total of 4.030 milligrams of radium compared to 0.0939 milligrams in the barium-rich products. If a greater recovery of radium from the barium-rich products is desired, additional fractionation steps would be required. After equilibrium was established a constant weight of radium (0.0521 milligram) was retained in the various fractions. In these experiments it amounted to 1.2 per cent of the radium processed. However, on continued operation, this percentage decreases with the quantity of radium processed.

TABLE VIII

SUMMATION OF THE RADIUM IN THE COUNTERCURRENT BATCH SYSTEM

	RADIUM (mg.)	PER CENT OF THE TOTAL RADIUM
RADIUM-RICH PRODUCTS	4.030	94.3
BIARIUM-RICH PRODUCTS	0.0939	2.2
FRACTIONS A_2 , A_1 , A_0 , A_{-1} , AND A_{-2}	0.0521	1.2*
NITRATE RESIDUE	0.1376	3.2
CHROMATE RESIDUE	0.0054	0.1
NITRIC ACID DISTILLATE	0.0000	0.0
TOTAL	4.319	101.0
ORIGINAL	4.270	100.0

* PER CENT RETENTION OF RADIUM INVERSELY PROPORTIONAL TO THE AMOUNT OF MATERIAL WORKED.

The radium in the various fractions and products accounted for only 97.7 per cent of the total. The remainder of the radium was in the hot nitric acid extracts. However, upon cooling these extracts 58.89 milligrams of barium nitrate crystallized from the solution. This nitrate residue contained 0.1376 milligram of radium or 3.2 per cent of the total radium. The radium in the nitrate residue may be recovered by dissolving the residue in water and using the solution as part of the reaction mixture in the subsequent fractionation step.

The total volume of the nitric acid extracts was 586 milliliters. After filtration of the nitrate residue 550 milliliters of this extract was distilled at $118 \pm 3^\circ\text{C}$. The clear, nitric acid distillate was radium free but the chromate residue contained 0.0054 milligram of radium. The percentage of the total radium in this chromate residue was only 0.13 per cent. Even this small amount of radium is not to be considered a radium loss since the chromate residues may be added to the various fractions as a substitute for potassium dichromate.

The total quantity of radium accounted for in Table VIII is slightly more than that in the original sample. However, since the analytical method²⁰ for the determination of radium is good only within three per cent, the results are satisfactory.

The purpose of the third series of experiments was to study further the radium losses. The barium-rich products obtained from the first series of experiments served as the starting sample and had a Ba:Ra ratio of 3,016,000:1. Large volumes of solution would have been required to work this low radium-content material by the procedure as outlined. Therefore, the volumes were reduced to one-third because enrichment studies indicated that a barium concentration as high as 30 grams of barium per liter could be used without reducing the radium enrichment per step.¹⁶ After three fractionation steps, the barium-enriched products were analyzed. These contained about 0.1 per cent of the total radium fractionated in the first series of experiments and had an average Ba:Ra ratio of 121,700,000:1. The radium content of this final product was determined by gamma counting since the conventional alpha slide method is impractical for samples of such low radium content.

A combination of the three series of experiments suggests a system in which there can be at least six fractionation steps on both the radium-enrichment and radium-depletion sides. An experimental system of this type is shown in Figure 9. For comparison, a calculated system based on a radium enrichment of 3.55 per fractionation step is included. It is evident that the composition of the various fractions in any given fractional chromate system can be accurately predicted and that the radium losses can be negligibly small, amounting to, at most, a few tenths of one per cent of the total radium.

INTERFERENCES

The reaction mixtures should be free of anions which form insoluble salts with barium and cations which form insoluble chromates. Lead was found to interfere with the process. It concentrates in the radium fractions and, therefore, must be removed. The interference of lead in the purification of radium is shown in the following experiment.

A barium-radium mixture containing 427.7 milligrams of barium and 8.153 milligrams of radium (Ba:Ra = 52.4:1) was obtained by the countercurrent batch process described above. This mixture without further lead purification was the starting material for three additional fractionation steps using the chromate-cyanate method at 0°C . At each step sufficient chromate was added to precipitate approximately 20 per cent of the total alkaline earths. The analyses of the fractions for barium and radium are given in Table IX.

For the first two fractionation steps the radium enrichment factors of 4.09 and 4.16, respectively, are comparable with the average enrichment factor of 4.26 for the chromate-cyanate method at 0°C . However, in the third fractionation step the enrichment factor is only 1.82 because of interference from lead. Apparently, lead chromate is more insoluble than radium chromate and, since insufficient soluble chromate was added to precipitate both the lead and the radium, a large fraction of the radium remains in the filtrate.

CONCENTRATION OF RADIUM BY THE CHROMATE-CYANATE METHOD AT 25° C

TABLE IX
INTERFERENCE OF LEAD IN THE CONCENTRATION OF RADIUM
BY THE CHROMATE-CYANATE METHOD AT 0°C.

FRACTION	BARIUM* (mg.)	RADIUM (mg.)	Ba:Ra RATIO	ENRICHMENT FACTOR
ORIGINAL	427.7	8.153	52.4:1	-
1	83.76	6.550	12.8:1	4.09
2	15.00	4.880	3.08:1	4.16
3	4.41	2.606	1.69:1	1.82

* DETERMINED BY DIFFERENCE AND NOT CORRECTED FOR LEAD.

The fractions were recombined and converted to nitrates so that the amount of lead in the starting mixture could be determined. Lead was separated as sulfide from a solution of these nitrates and was determined as sulfate. The weight of lead in the starting mixture was 12.1 milligrams or the mixture was 2.7 per cent lead. Since the lead concentrates in the precipitates at a rate probably greater than that for radium, it is apparent that in Fraction 3 a large percentage of the weight originally attributed to barium (4.41 milligrams) was actually lead.

As a final step in the purification of the barium-radium mixture (Ba:Ra = 100,000:1) obtained from the uranium residues, lead was removed by a sulfide precipitation.²² Spectrographic analysis indicated that the purified mixture contained only a trace of lead. Nevertheless, radium-enriched mixtures, which are obtained by a number of fractional chromate precipitations, need additional lead purification before being used as starting material for the preparation of pure radium.

MODIFICATIONS

Procedures for separation of radium and barium may be used in which the chromate precipitations are made at temperatures other than 25°C and alkaline earth concentrations other than 10 grams per liter. If the precipitations are carried out at 0°C, the enrichment factor per fractionation step for this countercurrent batch scheme is 4.26 compared to 3.55 at 25°C. However, precipitation at 0°C requires the use of refrigeration. If the fractions are large, as is true for radium-poor mixtures, manipulation at 0°C is more difficult and expensive than at 25°C. Precipitation at 0°C would be most useful for the final purification steps of radium from radium-rich mixtures. Precipitation at 100°C would be less expensive than at 25°C, since urea may be substituted for potassium cyanate. Precipitation at 100°C would be useful for reworking the radium-depleted mixtures. Unfortunately, at this high temperature the coefficient of enrichment per fractionation step is only 3.00. The amounts of reagents required for chromate procedures at 100°, 25°, and 0°C are given in Table X. It is assumed that the fractions have previously been built up to equilibrium weights from constant A_0 fractions of 100 parts of barium. It seems that the best procedure would require that the precipitations be made at

more than one temperature depending upon the characteristic most useful in the various parts of the fractionation scheme.

TABLE X

REAGENT DATA AT EQUILIBRIUM FOR THREE CHROMATE PROCEDURES

CHROMATE-UREA PROCEDURE AT 100°C

REAGENTS	UNITS	A_2	A_1	A_0	A_{-1}	A_{-2}
Ba ⁺⁺	g	10	32.5	100	97.5	90.0
K ₂ Cr ₂ O ₇	g	2.678	8.704	0.67	2.01	6.02
HNO ₃	ml	4	13	51.75	51.45	50.5
UREA	g	60.0	195	600.0	300.0	
TOTAL VOL.	ml	1,000	3,250	10,000	10,000	10,000

CHROMATE-CYANATE PROCEDURE AT 25°C

Ba ⁺⁺	g	7.369	27.85	100	98.86	94.81
K ₂ Cr ₂ O ₇	g	1.577	5.960	0.25	0.87	4.46
HNO ₃	ml	2.947	11.14	49.28	48.90	46.94
HOAc	ml	7.369	27.85	100		
KCNO	g	3.685	13.93	50.0	50.0	50.0
TOTAL VOL.	ml	736.9	2,785	10,000	10,000	10,000

CHROMATE-CYANATE PROCEDURE AT 0°C

Ba ⁺⁺	g	5.236	23.27	100	99.00	95.8
K ₂ Cr ₂ O ₇	g	0.9535	4.237	0.18	0.58	3.32
HNO ₃	ml	2.094	9.31	47.90	47.65	46.20
HOAc	ml	5.236	23.27	100		
KCNO	g	2.618	11.63	50.0	50.0	50.0
TOTAL VOL.	ml	523.6	2,327	10,000	10,000	10,000

The quantities of reagents used per fractionation step are volume dependent. If the concentration of barium (g./l.) is increased it is obvious that smaller containers could be used. Smaller quantities of nitric acid, potassium cyanate, and acetic acid are required at each step in the fractionation series, as is evident from the reagent data at the several barium concentrations given in Table XI.

TABLE XI

REAGENT DATA FOR THE CHROMATE-CYANATE METHOD
AT 25°C USING SEVERAL BARIUM CONCENTRATIONS

CONC. BARIUM (g/l)	REAGENTS	UNITS	A ₂	A ₁	A ₀	A ₁	A ₂
5	Ba ⁺⁺	g	7.369	27.85	100.0	98.86	94.81
	K ₂ Cr ₂ O ₇	g	1.577	5.960	0.25	0.87	4.46
	HNO ₃	ml	5.894	22.28	89.25	88.90	86.94
	HOAc	ml	14.738	55.70	200.0		
	KCNO	g	7.370	27.86	100.0	100.0	100.0
	TOTAL VOL.	ml	1,470.0	5,570.	20,000	20,000	20,000
10	Ba ⁺⁺	g	7.369	27.85	100.0	98.86	94.81
	K ₂ Cr ₂ O ₇	g	1.577	5.960	0.25	0.87	4.46
	HNO ₃	ml	2.947	11.14	49.28	48.90	46.94
	HOAc	ml	7.369	27.85	100		
	KCNO	g	3.685	13.93	50.0	50.0	50.0
	TOTAL VOL.	ml	737.	2,790	10,000	10,000	10,000
20	Ba ⁺⁺	g	7.369	27.85	100.0	98.86	94.81
	K ₂ Cr ₂ O ₇	g	1.577	5.960	0.25	0.87	4.46
	HNO ₃	ml	1.473	5.57	29.28	28.90	26.94
	HOAc	ml	3.685	13.93	50		
	KCNO	g	1.843	6.97	25.0	25.0	25.0
	TOTAL VOL.	ml	369.	1,390	5,000	5,000	5,000
30	Ba ⁺⁺	g	7.369	27.85	100.0	98.86	94.81
	K ₂ Cr ₂ O ₇	g	1.577	5.960	0.25	0.87	4.46
	HNO ₃	ml	0.982	3.71	22.61	23.23	20.27
	HOAc	ml	2.456	9.28	33.3		
	KCNO	g	1.228	4.64	16.67	16.67	16.67
	TOTAL VOL.	ml	246	928	3,330	3,330	3,330

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The procedures given in this report have utilized potassium cyanate as an internal reactant for the neutralization of nitric acid. However, sodium cyanate may be substituted for the potassium salt. The cost of sodium cyanate is considerably less than that of potassium cyanate, and because of its lower formula weight as compared to the potassium salt, only four-fifths as much sodium cyanate by weight is required per fractionation step.

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SECTION IV
COMPARISON OF THE CHROMATE METHOD WITH FRACTIONAL CRYSTALLIZATION

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The principal commercial methods^{1,4,6,7} for the recovery of radium from its ores, require that barium and radium be separated by fractional crystallization. The salts usually employed are the chlorides or the bromides. The practicability of the chromate (countercurrent batch) method can be realized only by a comparison with these older methods. The factors which must be considered are: (1) control of precipitating conditions, (2) simplicity, (3) enrichment per fractionation step, (4) speed of operation, (5) liquid volume size, and (6) chemical costs.

CONTROL OF PRECIPITATION CONDITIONS

The fraction of barium precipitated at each fractionation step is accurately controlled in the chromate method by the amount of alkali chromate or dichromate added to the reaction mixtures. Control of the fraction crystallized is more difficult in the fractional crystallization procedures, since it depends, in part, on the cooling conditions.

The following experiment indicates some of the difficulties which may arise as a result of lack of control of crystallizing conditions. A barium-radium bromide mixture containing 164.7 grams of barium and 1.697 milligrams of radium was fractionally crystallized in 0.33 normal hydrobromic acid. The fractionation mixtures were heated at their boiling temperature in beakers until saturated (as evidenced by the formation and persistence of crystals when the surface of the solution was blown with a stream of cool air). The beakers were covered, and the crystallizing mixtures allowed to cool to room temperature and stand for 24 hours. In each case the supernatant liquid was removed by decantation and analyzed for radium. The crystals were weighed to determine the fraction of barium crystallized.

The fractionation scheme is shown in Figure 10. The circles represent the individual fractions each of which yields a crystalline phase and a liquid phase. Crystalline and liquid phases which were combined to form a new fraction are shown as components of a common circle. The liquid phases are represented by the top half of the circles and the crystalline phases by the bottom half. The numbers shown in the top half of the circles are the relative radium concentrations in the various liquid phases compared to an arbitrary original concentration of 1.00 while the values in the bottom half are those of the crystalline phases. Calculated values are shown in italics to differentiate them from the experimental values. The agreement between the experimental and calculated values for many phases is not particularly good. Frequently, phases of widely different radium concentrations were combined, whereas, theoretically, only phases of the same composition are combined. Furthermore, there is no fraction which repeats the same composition as the original sample. Therefore, failure to control accurately the crystallization conditions partially disrupts the system and results in a less efficient system. The low sensitivity of the gamma-counting method for radium doubtless accounts for the inconsistent results in the fractions of extremely low radium content.

SIMPLICITY

In a countercurrent batch fractionation scheme such as the triangular type shown in Figure 1 (Section I), the more frequently fractions of equal compositions recur, the simpler the fractionation system. The chromate procedure described in this report is the simplest countercurrent batch fractionation system possible, since, as discussed in Section I, Fraction 2b is the first repeating fraction. In the more complicated chloride and bromide procedures, Fractions 3b and 5c, respectively, are the first repeating fractions.

BROMIDE FRACTIONAL
CRYSTALLIZATION SCHEME

The chloride fractional crystallization procedure⁴ is based on the fact that, when a saturated chloride solution is allowed to cool from 100°C to room temperature, approximately 50 per cent of the barium-radium chloride mixture crystallizes. In each crystallization step about 80 per cent of the total radium is contained in these mixed chlorides, and the enrichment factor for each fractionation step is 1.6 ($80 \div 50$). The bromide fractional crystallization procedure² is based on an enrichment factor of 2.5 per crystallization step. If a 0.33 normal hydrobromic acid solution is saturated at 100°C with a barium-radium bromide mixture, approximately 33.3 per cent of the mixture containing 83.1 per cent of the total radium crystallizes when the solution is allowed to cool to room temperature.

ENRICHMENT PER FRACTIONATION STEP

Enrichment factors of somewhat less than 1.6 are usually assigned to the fractional chloride system while a factor of 2.0 to 2.2 is more frequently used for the acid-bromide systems.⁴ An enrichment factor of 3.55 per fractionation step (Table IV) is obtained when the chromate procedure at 25°C is utilized. It must be emphasized that the greater the enrichment per fractionation step the fewer the total number of steps required for the separation of radium.

A decrease in enrichment factor per fractionation step has been reported for the fractional crystallization of radium-rich mixtures due to the formation of double salts of barium and radium halides,^{2,21} such as $\text{RaBr}_2 \cdot 2\text{BaBr}_2 \cdot 6\text{H}_2\text{O}$. No such decrease in enrichment has been found for chromate mixtures.¹⁶

SPEED OF OPERATION

The separation of radium from barium can be made with greater rapidity by the fractional chromate procedure since fractional crystallization methods usually require that, to allow for the attainment of equilibrium conditions, each fraction be crystallized no more than once a day. No such restrictions are involved in fractional precipitation. Precipitations may be made consecutively, each precipitation requiring about one hour.

LIQUID VOLUME SIZE

The principal advantage of fractional crystallization is that high salt concentrations are used, whereas relatively dilute solutions are used in the chromate procedures. The halides are much more soluble than the nitrate (the salt which limits the barium-radium concentration in the chromate procedure). Therefore, considerably smaller containers may be used for fractional crystallization and the initial container costs would be correspondingly less. However, for radium-poor mixtures ($\text{Ba}:\text{Ra} > 100,000:1$) the concentration of barium-radium salts can be greatly increased by using the chromate-urea method at 100°C, since the nitrate is considerably more soluble in hot solutions than in cold solutions. For radium-rich mixtures ($\text{Ba}:\text{Ra} < 100:1$) the small volume resulting from the high salt concentrations used in fractional crystallization is a disadvantage.

CHEMICAL COSTS

The only reagent required for fractional crystallization is hydrochloric or hydrobromic acid, most of which can be recovered for reuse. For the chromate precipitation

methods the reagents required are nitric acid, acetic acid, a source of chromate ions, and urea or a cyanate. The internal reactant is of course destroyed. Most of the other reagents may be recovered, if their recovery is economically practical. An evaluation of the recovery of these reagents is required before an accurate comparison with fractional crystallization can be made.

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APPENDIX

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APPENDIX A

SOLUTION OF EQUATIONS FOR REPEATING CONCENTRATIONS (See Section I)

A trigonometric substitution method was used for the solution of fourth and higher degree equations obtained for repeating composition in Fractions 4b, 5b, and 5c. Taking the trigonometric relationship,

$$\sin^2 \theta = 1 - \cos^2 \theta$$

a simplification substitution can be made by letting

$$y = \cos^2 \theta \text{ and } 1 - y = \sin^2 \theta$$

Applying this to the fifth degree equation obtained for repeating composition in Fraction 5c,

$$y^3 (1 - y)^2 = x^3 (1 - x)^2$$

one obtains the equation

$$(\cos^2 \theta)^3 (\sin^2 \theta)^2 = x^3 (1 - x)^2 = f(x)$$

or

$$\cos^6 \theta \sin^4 \theta = f(x)$$

Taking logarithms the equation becomes,

$$6 \log \cos \theta + 4 \log \sin \theta = \log f(x)$$

and by dividing by 4,

$$1.5 \log \cos \theta + \log \sin \theta = \frac{\log f(x)}{4}$$

where

$$f(x) = x^3 (1 - x)^2$$

From tables of logarithms of trigonometric functions, the value of θ can be rapidly evaluated for any specific value of x . The corresponding value of y is found from $y = \cos^2 \theta$.

The equations for operating lines for repeating compositions in fractions of the third, fourth, and fifth rows of the fractionation scheme are summarized in Table XII. Solutions of the operating line equations for selected values of x are given in Table XIII. The operating lines shown in Figure 2 (Section I) were plotted from these values.

TABLE XII
EQUATIONS FOR OPERATING LINES

REPEATING FRACTION	EQUATION FOR OPERATING LINE	TRIGONOMETRIC FORM OF THE EQUATIONS
3b	$y^2 (1 - y) = x^2 (1 - x)$	$2 \log \cos \theta + \log \sin \theta = \frac{\log f(x)^*}{2}$
4b	$y^3 (1 - y) = x^3 (1 - x)$	$3 \log \cos \theta + \log \sin \theta = \frac{\log f(x)}{2}$
5b	$y^4 (1 - y) = x^4 (1 - x)$	$4 \log \cos \theta + \log \sin \theta = \frac{\log f(x)}{2}$
5c	$y^3 (1 - y)^2 = x^3 (1 - x)^2$	$1.5 \log \cos \theta + \log \sin \theta = \frac{\log f(x)}{4}$
3c	$y (1 - y)^2 = x (1 - x)^2$	$\log \cos \theta + 2 \log \sin \theta = \frac{\log f(x)^*}{2}$
4d	$y (1 - y)^3 = x (1 - x)^3$	$\log \cos \theta + 3 \log \sin \theta = \frac{\log f(x)}{2}$
5e	$y (1 - y)^4 = x (1 - x)^4$	$\log \cos \theta + 4 \log \sin \theta = \frac{\log f(x)}{2}$
5d	$y^2 (1 - y)^3 = x^2 (1 - x)^3$	$\log \cos \theta + 1.5 \log \sin \theta = \frac{\log f(x)}{4}$

* TRIGONOMETRIC SUBSTITUTION WAS NOT USED TO SOLVE THE EQUATIONS FOR FRACTIONS 3b AND 3c, SINCE THESE MAY BE REDUCED TO A QUADRATIC FORM.

TABLE XIII
SOLUTIONS OF EQUATIONS FOR OPERATING LINES

3b		4b		5b		5c	
x	y	x	y	x	y	x	y
0.10	0.99083	0.25	0.98784	0.30	0.99420	0.10	0.97026
0.25	0.9478	0.35	0.9685	0.40	0.98359	0.20	0.91875
0.30	0.9265	0.40	0.9561	0.50	0.96378	0.30	0.85434
0.40	0.875	0.50	0.9196	0.60	0.93099	0.40	0.77941
0.50	0.809	0.60	0.8678	0.70	0.87978	0.50	0.69471
0.60	0.729	0.70	0.79593	0.85	0.74280	0.70	0.49408
0.70	0.632	0.80	0.69510	0.90	0.66549	0.80	0.37397
0.80	0.5123	0.90	0.54190	0.98	0.42283	0.90	0.23102
0.90	0.354	0.95	0.41955				
0.95	0.2443	0.98	0.29951				

SOLUTIONS FOR OPERATING LINES FOR FRACTIONS 3c, 4d, 5e, AND 5d WERE OBTAINED FROM THE ABOVE SOLUTIONS BY THE COMPLEMENTARY RELATIONSHIPS $y = 1 - x$ AND $x = 1 - y$.

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MAXIMUM ENRICHMENT FOR A SYSTEM FOLLOWING THE LOGARITHMIC DISTRIBUTION LAW

The enrichment, y/x , for a single precipitation is greatest for small values of x . The maximum value is obtained as x approaches zero and can be shown to be equal to λ , the distribution constant, by the following consideration. Solving the Doerner and Hoskins equation for y ,

$$y = 1 - (1 - x)^\lambda$$

and dividing by x gives the enrichment, y/x , in terms of the ratio of two functions of x .

$$\frac{y}{x} = \frac{1 - (1 - x)^\lambda}{x} = \frac{f(x)}{F(x)}$$

The limit of this ratio as x approaches zero is indeterminate but can be evaluated by finding the limit of the ratio of the first derivatives of the two functions as x approaches zero.

$$\lim_{x \rightarrow 0} \frac{y}{x} = \lim_{x \rightarrow 0} \frac{f'(x)}{F'(x)} = \frac{\lambda(1 - x)^{\lambda-1}}{1} = \lambda$$

The limiting value of the enrichment is therefore equal to λ , the distribution constant.

APPENDIX B

PROCEDURE FOR THE CHROMATE FRACTIONAL PRECIPITATION PROCESS

A general procedure for the countercurrent batch fractional precipitation process was given in Section III. A more specific procedure for each fractionation step is described below. Reagent data for building up the system is given in Table V, which is based on A_0 fractions of 100 parts of barium. The amounts of reagents for any other size system can be calculated from these tabulated values. After equilibrium is established the quantities of the various reagents used in each fractionation step remains constant and are given in the last line of Table V.

Fraction A_0

Fraction A_0 is composed of the precipitate from A_{-1} , the filtrate from A_1 , and original material. (In the initial fractionation series 100 parts of original barium-radium mixture is used.) To this mixture is added enough nitric acid to dissolve completely the barium chromate and to make the final solution 0.06 normal with respect to nitric acid. The solution is diluted with water until it is one per cent with respect to barium, and sufficient glacial acetic acid is added so that the solution is one per cent with respect to this acid. Potassium dichromate, equivalent to 20 per cent of the total barium present, is then added. To this solution is added, with stirring, 5 grams of potassium cyanate for each liter of solution. The precipitation is allowed to continue until the supernatant liquid is nearly colorless and the mixture is then filtered. The precipitate is saved for A_1 and the filtrate for A_{-1} .

Fraction A_1

Fraction A_1 is composed of the filtrate from A_2 and the precipitate from A_0 . The total amount of chromate present is more than enough to precipitate 20 per cent of the total barium. Therefore, the barium-radium chromate from A_0 is converted to nitrate by extraction with hot concentrated nitric acid. (The extraction requires 10 milliliters of concentrated nitric acid per gram of chromate. A general procedure for nitric acid extractions was given in Section III.) The nitrate is dissolved in hot water and combined with the filtrate from A_2 . To this solution is added sufficient nitric acid and water to make the final solution 0.06 normal in nitric acid and one per cent in barium. After the addition of acetic acid to make the solution one per cent in this acid, enough potassium dichromate is added to precipitate 20 per cent of the total barium. Finally the potassium cyanate (5 grams per liter) is added. When the precipitation is complete, as evidenced by a nearly colorless supernatant, the mixture is filtered. The precipitate is saved for A_2 and the filtrate is saved to be added to the subsequent A_0 fraction.

Fraction A_2

Fraction A_2 consists of the precipitate from A_1 only. This precipitate must be extracted with hot concentrated nitric acid to convert it to nitrate. The nitrate is dissolved in water (sufficient water is used so that the final solution contains one per cent of barium). Enough nitric and acetic acids are added so that the final solution is 0.06 normal in nitric acid and one per cent in acetic acid. Potassium dichromate equivalent to 20 per cent of the total barium is then added followed by the addition of 5 grams of potassium cyanate per liter of solution. The reaction mixture is stirred, and after precipitation is complete, the mixture is filtered. The precipitates from A_2 are collected and serve as starting material for further radium concentration.

Fraction A_1

The precipitate from A_2 is dissolved in hot nitric acid (one part acid to three parts of water) and added to the filtrate from A_0 . The final reaction solution should be 0.06 normal with respect to nitric acid. Potassium dichromate is added so that the total chromate ion present is sufficient to precipitate 20 per cent of the barium. To the reaction mixture, finally, is added potassium cyanate (5 grams per liter) and the reaction is allowed to continue with stirring until the supernatant liquid is nearly colorless. The mixture is then filtered and the precipitate is saved for A_0 and the filtrate is saved for A_2 .

Fraction A_2

Fraction A_2 is composed of the filtrate from A_1 only. Sufficient nitric acid is added to make this filtrate 0.06 normal with respect to nitric acid. Potassium dichromate to precipitate 20 per cent of the barium is added. Potassium cyanate (5 grams per liter) is finally added to the reaction mixture and precipitation is allowed to continue with stirring until the supernatant liquid is nearly colorless. The mixture is then filtered and the precipitate is saved for A_1 in the subsequent fractionation series. The filtrate is heated to boiling and the alkaline earths precipitated as the carbonates. These carbonates are filtered, dried, and saved as starting material for subsequent treatment if a greater radium recovery is required.