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The Radiochemistry of Radium

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CHEMISTRY

The Radiochemistry of Radium

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FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of radiochemistry and nuclear chemistry. Support for the activities of this and other subcommittees of the Committee on Nuclear Science is provided by a grant from the National Science Foundation.

The Subcommittee has concerned itself with preparation of publications, encouraging and supporting activities in nuclear education, sponsoring symposia on selected current topics in radiochemistry and nuclear chemistry, and investigating special problems as they arise. A series of monographs on the radiochemistry of essentially all the elements and on radiochemical techniques is being published. Initiation and encouragement of publication of articles on nuclear education in various subject areas of chemistry have occurred, and development and improvement of certain education activities (e.g., laboratory and demonstration experiments with radioactivity) have been encouraged and assisted. Radioactive contamination of reagents and materials has been investigated and specific recommendations made.

This series of monographs has resulted from the need for comprehensive compilations of radiochemical and nuclear chemical information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or with a specialized technique. The U. S. Atomic Energy Commission has sponsored the printing of the series.

Comments and suggestions for further publications and activities of value to persons working with radioactivity are welcomed by the Subcommittee.

N. E. Ballou, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This monograph on the radiochemistry of radium is one in a series covering the radiochemistry of essentially all the elements. In it are included reviews of nuclear and chemical properties of radium, discussions of methods of sample dissolution and of separation reactions, descriptions of counting techniques, and a compilation of radiochemical separation procedures.

As new information accumulates on chemical and nuclear properties of radium and on separation and measurement techniques, consideration will be given to revision of this monograph. Consequently as further information becomes available in both published and unpublished form, readers are encouraged to bring it to the attention of the author for possible inclusion in future editions of this monograph.

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I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF RADIUM

G. Bouissières, Radium, Nouveau Traité de Chimie Minérale, IV, pp. 930-955, ed. by P. Pascal; Masson et Cie., Paris (1958). (175 references to November 30, 1955).

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*Mound Laboratory is operated by Monsanto Research Corporation for the U. S. Atomic Energy Commission under Contract Number AT-33-1-GEN-53

J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Chapter XXVI, pp. 53-154. Longmans, Green and Co., London (1946). References to 1922.

S. B. Schwind and F. E. Croxton, "Radium. A Bibliography of Unclassified Literature," U. S. Atomic Energy Comm. Rpt. TID-363 (July, 1950). Contains 745 references covering the period 1898 to 1950, mostly with abstracts. Indexed as to subjects, authors, patent numbers and report numbers.

J. Sedlet, "Radon and Radium," Chapter in Part II of "Treatise on Analytical Chemistry" edited by I. M. Kolthoff and P. J. Elving with the assistance of E. B. Sandell. Interscience Publishers, New York. To be published. (approximately 350 references through 1963)

II. TABLE I - ISOTOPES OF RADIUM

Mass	Mode of Decay	Half Life		Source
213	α	2.7	min	Th + p; Pb + C^{6+}
219	α	$\sim 10^{-3}$	sec	daughter Th^{223}
220	α	$\sim$ 0.03	sec	daughter Th^{224}
221	α	30	sec	daughter Th^{225}
222	α	38	sec	daughter Th^{226}
223 (AcX)	α	11.435	days	Natural; descendant U^{235}
224 (ThX)	α	3.64	days	Natural; descendant Th^{232}
225	β^-	14.8	days	daughter Th^{229}
226	α	1622	years	Natural, descendant U^{238}
227	β^-	41.2	min	$Ra^{226}(n,\gamma)$
228 ($MsTh_1$)	β^-	6.7	years	Natural; descendant Th^{232}
229	β^-	$\sim$ 1	min	daughter Th^{233}
230	β^-	1	hour	Th + d

III. REVIEW OF THOSE FEATURES OF RADIUM OF CHIEF INTEREST TO RADIOCHEMISTS

1. Metallic Radium

Radium metal was prepared by Curie and Debierne[1] by electrolysis of a radium chloride solution using a mercury cathode and a platinum-iridium anode. The resulting amalgam was thermally decomposed in a hydrogen atmosphere leaving a residue of pure radium metal. The metal has also been prepared by thermal decomposition of radium azide, $Ra(N_3)_2$.[2]

Freshly prepared radium metal has a brilliant white metallic luster but rapidly becomes black on exposure to air supposedly because of the formation of a nitride. Chemically, the metal is highly electropositive. It reacts readily with water, evolving hydrogen and forming a soluble hydroxide. The calculated heat of reaction is approximately 9.0 Kcal./g. atom. Metallic radium has a melting point of 700°C[1] or 960°C[3] and a boiling point of 1140°C.[3] It has a specific gravity of approximately 5.0. The standard oxidation potential for the $Ra(s)-Ra^{++}$ couple is probably close to that of barium, namely, $E^\circ = +2.90$ volts.

2. Soluble Salts of Radium

Radium is an alkaline earth element with chemical properties very similar to those of barium. The element exhibits only one oxidation state (+2) in solution. Because of its highly basic character, the divalent ion is not easily complexed. Hence, most radium compounds are simple ionic salts, which are white when freshly prepared, turning yellow and ultimately dark with age owing to self-decomposition from the alpha radiation.

The chloride, bromide, and nitrate of radium are soluble in water, but their solubilities decrease with increasing concentration of the respective mineral acid. Radium chloride and bromide are less soluble than the corresponding barium salts but radium nitrate is more soluble than barium nitrate.[9] These compounds are frequently used in fractional crystallization and precipitation methods for the separation of barium and radium.

Radium hydroxide is the most soluble of the alkaline earth hydroxides and more basic than barium hydroxide. It is more soluble than actinium and thorium hydroxides and can be separated from these elements by their precipitation with ammonia.

Chloride Radium chloride is a colorless and spontaneously luminous compound which gradually becomes yellowish as it ages. When small quantities of barium impurity are present the crystals of radium chloride sometimes have a rose color. When crystallized from aqueous solution the compound forms a dihydrate, $RaCl_2 \cdot 2H_2O$, which is isomorphous with $BaCl_2 \cdot 2H_2O$. Pure anhydrous radium chloride was prepared by Hönigschmid[4] in his classical determination of the atomic weight of radium. The anhydrous chloride is prepared by heating radium bromide in a stream of dry hydrogen chloride or by dehydrating radium sulfate in a current of dry air at 300°C and then bringing the dry sulfate to red heat in a current of hydrogen chloride and carbon tetrachloride in a quartz tube.

Anhydrous radium chloride has a density of 4.9[5] and a melting point of about 900°C.[6] Radium chloride is feebly paramagnetic having a magnetic susceptibility of +1.05 x 10^6 (unlike barium chloride, which is diamagnetic).[7] Radium chloride burns with a carmine red flame (again unlike barium, which burns with a green flame). The spectrum is composed of two bright lines in the red region of the spectrum, one bright line in the blue, and two fainter ones in the violet.[8]

The solubility of radium chloride is 24.5 grams per 100 grams of water[9], whereas that of barium chloride is 30.7 grams per 100 grams of water at 25°C.[10] This difference in solubility is the basis for the fractional separation of the two elements.

The difference is greater in hydrochloric acid solutions, because the solubility of radium chloride decreases more rapidly with increasing acid concentration than does that of barium chloride. However, the enrichment per fractional crystallization step decreases for barium-radium mixtures highly concentrated in radium because of double salt formation between the two chlorides. Final separation of radium from barium has customarily been carried out by fractional crystallization of the bromides.

Radium chloride is insoluble in a mixture of ice-cold 37% hydrochloric acid and ether (6:1 v/v).[59]

<u>Bromide</u> Radium bromide crystallizes from aqueous solutions as a dihydrate which is isomorphous with the barium compound $BaBr_2 \cdot 2H_2O$. The crystals belong to the monoclinic system. Hönigschmid[11] prepared pure anhydrous radium bromide by dehydrating the dihydrate in a stream of dry air at 200°C. It has also been prepared by heating radium chloride to red heat in a stream of dry hydrogen bromide gas.[5] Radium bromide melts at 728°C [12] and decomposes at higher temperatures, finally forming an insoluble glass. The density of the anhydrous salt is 5.78.[13]

Crystals of radium bromide occasionally explode. The accumulation of helium gas within the crystals weakens them causing rupture. When radium bromide is sealed in a glass tube for six months or more a sufficient difference in electrical potential may build up between the salt and glass tube to cause an explosion when the tube is touched with a file. The gradual chemical decomposition of the compound in a sealed tube is evident from the detectable liberation of bromine. The air immediately surrounding a sample of radium bromide glows and shows all of the bands in the nitrogen spectrum. The luminosity is probably due to the impact of the α radiation on the nitrogen molecules of air.

Radium bromide is considerably more soluble than the chloride; its solubility is 70.6 grams in 100 grams of water. Although the difference between the solubilities of radium and barium bromides is less than for the chlorides, the bromides offer a more efficient system for separation by fractional crystallization. When the radium concentration in the mixture with barium is 20 milligrams per kilogram, one fractional crystallization step with the bromides is about equal to two for the chlorides.

Radium bromide is insoluble in a 4:1 (v/v) mixture of 47% HBr and methyl alcohol[60].

Nitrate Radium nitrate is a white compound most conveniently prepared by dissolving radium carbonate in nitric acid. The compound is soluble in water to the extent of 13.9 grams per 100 grams of water[9]. The solubility of radium nitrate in aqueous solution decreases with increasing concentration of nitric acid. The very low solubility of radium nitrate in 80% nitric acid is useful in its separation from most other elements.

3. Insoluble Salts of Radium - Precipitation and Coprecipitation Characteristics

Radium yields the same types of insoluble compounds as does barium, the better known of which are shown in Table II. In addition to those listed, the phosphate, oxalate, and sulfite coprecipitate with the corresponding barium compounds and are probably themselves insoluble.

Most of the compounds of radium are more insoluble than the corresponding barium compounds and concentrate in the precipitate upon fractional precipitation of barium-radium mixtures. One notable exception is radium carbonate, which is more soluble than barium carbonate and, hence, concentrates in the soluble fraction (filtrate) when barium-radium carbonate mixtures are fractionally separated.

Radium coprecipitates with all barium compounds (and to a lesser extent with most strontium and lead compounds) even though the solubility product of the radium compound itself may not be exceeded. Because radium was one of the first radioactive elements utilized in tracer research, it was used in the development of the coprecipitation laws.

TABLE II - INSOLUBLE COMPOUNDS OF RADIUM

Reagent	Precipitate	Solubility in Water	Solubility in Other Reagents
$SO_4^=$	$RaSO_4$	2.1 x 10^{-4} g/100g @ 20°C, S.P. = 4.25 x 10^{-11}, less soluble than $BaSO_4$	Insoluble in dilute acids, soluble in concentrated sulfuric acid, converted to $RaCO_3$ by fusion with sodium carbonate
$CrO_4^=$	$RaCrO_4$	Very insoluble, less soluble than $BaCrO_4$	Soluble in strong acids ($>1\underline{N}$), insoluble in hot dilute sodium carbonate solutions
$CO_3^=$	$RaCO_3$	Insoluble, more soluble than $BaCO_3$	Soluble in dilute acids, more soluble in concentrated ammonium carbonate solution than $BaCO_3$
IO_3^-	$Ra(IO_3)_2$	0.176 g/l @ 0°C 0.437 g/l @ 25°C 1.244 g/l @ 78°C 1.705 g/l @ 100°C	
$BeF_4^=$	$RaBeF_4$	Probably less soluble than $BaBeF_4$	
NO_3^-	$Ra(NO_3)_2$	13.9 g/100 g	Insoluble in 80% HNO_3

Coprecipitation Laws A brief summary of the distribution laws which govern coprecipitation by isomorphous replacement will be of value in the discussion of insoluble radium compounds.

When a radium salt is coprecipitated with a barium salt, there are two systematic ways in which the radium may be distributed in the crystals. One type of distribution is expressed by the homogeneous distribution law of Henderson and Kracek[14] in which the ratio of the concentrations of radium to barium in the precipitated crystals is proportional to the ratio of the concentrations in the final solution:

$$\left(\frac{\mathrm{Ra}}{\mathrm{Ba}}\right)_{\text{crystals}} = D\left(\frac{\mathrm{Ra}}{\mathrm{Ba}}\right)_{\text{solution}} \qquad (1)$$

where D represents the homogeneous distribution coefficient. This distribution law indicates a state of true thermodynamic equilibrium in which the solid phase has been digested sufficiently to remove all concentration gradients and is homogeneous.

The second type of distribution is characterized by the logarithmic distribution law introduced by Doerner and Hoskins[15] and expressed by the following equation:

$$\log \frac{\text{total Ra}}{\text{Ra in solution}} = \lambda \log \frac{\text{total Ba}}{\text{Ba in solution}} \qquad (2)$$

where λ represents the logarithmic distribution coefficient. In this case a state of true thermodynamic equilibrium exists at all times between the solution and an infinitesimal surface layer on the crystal (but not with the crystal as a whole, which retains a radial concentration gradient).

If the thermodynamic system is restricted to the surface layer of the crystal and the solution in equilibrium, the two distribution laws become identical. Because it is difficult to measure the surface concentration around a crystal accurately, it is customary to analyze the crystal as a whole. Therefore, the simple distribution must be integrated over the period of crystal growth, which results in the logarithmic relationship. Bonner and Kahn[16] reviewed the literature and described the types of distribution obtained when a radium salt is coprecipitated with a barium salt under various precipitation conditions. For a given set of ideal conditions which lead to homogeneous distribution, the values calculated for D remain constant while those of λ decrease as the amount of barium salt precipitated increases. Conversely, for a set of ideal conditions which lead to logarithmic distribution, the values calculated for λ remain constant while those of D increase as the amount of barium salt precipitated increases.

Because it is difficult to maintain experimental conditions which exclusively favor one type of distribution, the distribution laws do not adequately describe much of the research that has been done on the distribution of radium in barium salts. Frequently, neither D nor λ is constant, but both show increasing or decreasing trends in value when the fraction of the barium salt crystallized or precipitated is increased.[17]

Nevertheless, the distribution laws are helpful in selecting a practical method for the fractional separation of barium and radium. Distribution coefficients greater than unity indicate that the radium is being concentrated in the precipitate, while those less than unity indicate concentration in the filtrate. The compound selected for the separation of radium from barium should be one which shows extreme values of D or λ.

Methods leading to the logarithmic distribution are more efficient than those leading to homogeneous distribution. For example, when the distribution coefficient is 10, precipitation of 50% of the barium removes 99.8% of the radium if it is logarithmically incorporated in the crystals, but only 90.9% if it is homogeneously incorporated.

In choosing an efficient carrier for a radioactive tracer, a material should be selected such that the distribution coefficient (either λ or D) is not less than 1.0.

<u>Sulfate</u> Radium sulfate is the most insoluble of the alkaline earth sulfates and probably the most insoluble radium compound known. Its solubility is 2.1 x 10^{-4} gram per 100 milliliters of water.[18] For this reason, precipitation as the sulfate is a common practice for the recovery of radium, particularly with the addition of barium carrier. Precipitation is readily accomplished by adding dilute sulfuric acid to a solution of a soluble radium compound. Radium sulfate may be dehydrated completely by heating it in dry air at 300°C. The compound is soluble in concentrated sulfuric acid, but precipitates upon dilution of the acid. It is converted to radium carbonate by fusion with sodium carbonate (a technique frequently used for

the dissolution of radiferous barium sulfate because the resulting barium-radium carbonates are soluble in any dilute mineral acid). Radium sulfate is reduced to the sulfide by ignition with calcium carbide, calcium hydride, and carbon. The resulting sulfide is soluble in either water or dilute acids. The sulfate has a good adsorptive capacity for radon isotopes, thus adding to its utility in the counting of samples. Mass absorption coefficients have been determined to correct for the absorption of the gamma radiation in $RaSO_4$ as well as $RaCl_2$, $RaBr_2$ and $RaCO_3$.[19]

Because of its great insolubility radium sulfate is less dangerous biologically than most radium compounds. It is widely used in the preparation of radium standards

From an investigation on the coprecipitation of radium with barium sulfate, Doerner and Hoskins[15] derived the logarithmic distribution law (Equation 2). Their work was later repeated by Gordon and Rowley[20] who utilized the technique of precipitation from homogeneous solution.[21] This technique affords a means for attainment of equilibrium between crystal surfaces and solution. Barium sulfate was precipitated from homogeneous solution by the hydrolysis of sulfamic acid in the presence of barium and radium ions. The distribution of radium between the aqueous and solid phases was observed to follow the logarithmic distribution law (i.e., λ was constant) over the range in which the percentage of the barium precipitated was varied from 3% to 96%.

At 90°C the value of λ was 1.21 but increased with decreasing temperature (t) according to the relationship:

$$\log_{10} \lambda = \frac{220}{273+t} - 0.520 \qquad (3)$$

Thus, barium sulfate is a better carrier for radium when precipitated from cold solutions than from hot solutions.

Barium sulfate is such an excellent carrier for radium that radium is quickly adsorbed even when preformed crystals of barium sulfate are added to a radiferous solution. At first, part of the adsorbed radium may be removed by washing the crystals, but after a short time the radium becomes incorporated into the crystal lattice and can no longer be removed by washing. The migration of the radium into the lattice of barium sulfate continues slowly until isomorphous mixed crystals are formed.[22]

Strontium sulfate coprecipitates radium in a way very similar to barium sulfate but somewhat less completely.[22] Lead sulfate is a moderately good carrier for radium.[23] Coprecipitation of radium on calcium sulfate is poor. Coprecipitation of radium with potassium sulfate, rubidium sulfate, and ammonium sulfate via anomalous mixed crystal formation has been observed.[24] Radium does not coprecipitate with most other sulfates.

<u>Chromate</u> Freshly prepared radium chromate is a yellowish compound resembling barium chromate. It is precipitated by adding a soluble chromate to a solution of a radium salt.

Precipitation from homogeneous solution has been achieved by gradually neutralizing a nitric acid solution of radium chromate using urea or potassium cyanate as an internal reactant to generate ammonia uniformly throughout the solution.[17] Radium chromate is soluble in mineral acids, but unlike barium chromate it is not converted to the carbonate on heating with dilute sodium carbonate solutions. Radium chromate is less soluble in most dilute acids than barium chromate but more soluble than lead chromate.[25] Treatment with hot concentrated nitric acid converts radium chromate to radium nitrate, which is insoluble in the concentrated nitric acid.

Nikitin[26] attempted to separate barium and radium chromates in a manner similar to that used for the separation of barium and strontium chromates. Instead of precipitating the chromates from an acetic acid solution as is done for the separation of barium and strontium, he chose a stronger acid, namely, trichloracetic acid. Although the separation is not quantitative it can serve over a narrow composition range for the concentration of radium.

From an investigation on the coprecipitation of radium with barium chromate, Henderson and Kracek[14] proposed the homogeneous distribution law (Equation 1). Barium-radium chromates were fractionally precipitated from nitric acid or hydrochloric acid solutions by neutralizing part of the acid with sodium hydroxide solution. The mixtures were allowed to stand several days before filtering the precipitated chromates, thus allowing time for the attainment of equilibrium between crystals and solutions. However, when the chromates were fractionally precipitated from homogeneous solution[17] the distribution of radium in the crystals followed the logarithmic distribution law (Equation 2). The separation of radium from barium is improved (i.e., the distribution coefficients are larger) if precipitations are made from cold solutions instead of hot solutions and if made from dilute acid solutions rather than neutral solutions.[27] But the separation is not affected by the composition (barium-radium ratio) of the original mixture or by the concentration of barium in solution. The distribution coefficient obtained for the fractional precipitation of the chromates is about equal to that obtained by fractional crystallization of the bromides but better than that for the fractionation of the chlorides, nitrates, or sulfates.

Fractional precipitation of the chromates from homogeneous solution has been used in a process for the separation of radium and barium.[25] Its principal advantages over the classical Curie process for separating radium and barium by fractional crystallization of the halides are: (1) greater radium enrichment per fractionation step, (2) better control of precipitation conditions, and (3) greater simplicity and speed of operation.

Radium is coprecipitated moderately well by lead chromate and silver chromate in the presence of an excess of chromate ions but is coprecipitated poorly in the presence of an excess of the respective metal ions.

Carbonate Nikitin[28] postulated that barium and radium carbonates would not form isomorphous mixed crystals because of a morphotropic conversion of their structures resulting from the fact that the radius of the radium ion is greater than the radius of the barium ion. While barium carbonate has a structure similar to that of aragonite, radium carbonate, according to Nikitin, should have a structure similar to that of rubidium nitrate. Nikitin determined the solubilities of barium and radium carbonates at room temperature in a concentrated solution of ammonium carbonate and ammonium chloride and found that radium carbonate is about 10 times more soluble than barium carbonate. The difference in solubility is greater than usually found for most barium and radium compounds.

Radium carbonate may be prepared by precipitation from neutral or weakly alkaline solutions of radium salts with a solution of ammonium carbonate. Gram quantities of radium have been recovered from a concentrated solution of radium nitrate by precipitation as the carbonate.[29] The radium nitrate solution was adjusted to pH 9.2-9.5 with concentrated ammonium hydroxide. Carbon dioxide gas was bubbled into the solution until the pH was just slightly above 7. To insure complete precipitation of radium carbonate, ethyl alcohol and some additional ammonium hydroxide solution were added. The radium carbonate was filtered and washed with 90% ethyl alcohol. The radium carbonate was first dried at 110°C to remove the alcohol, then ignited at 600°C and weighed as $RaCO_3$.

Mixtures of radium and barium have been separated by fractional precipitation from homogeneous solution as carbonates.[30]

Solutions of the mixed trichloroacetates were heated. Under the influence of heat the trichloroacetate ion hydrolyzes yielding chloroform and carbon dioxide. The chloroform is evolved from the hot solution. The carbon dioxide reacts with the water and any cation present to form a carbonate.[31] When a mixture of chemically similar cations such as radium and barium is present in the solution, the one which forms the least soluble carbonate concentrates in the precipitate. Consequently, for a radium-barium mixture radium is concentrated in the liquor and barium in the precipitate.

It appears that the separation of radium and barium by fractional carbonate precipitation is more efficient at higher temperatures. The logarithmic distribution coefficient (λ) at 90°C is 0.18[30] whereas at 20°C it is about 0.51.[32] Radium and barium carbonates probably show an increasing solubility differential with increasing temperature.

Separation of Radium from Other Elements (Except Barium)

Fresenius and Jande[33] recommend the following reactions for the separation of radium from all other elements (with the exception of barium)

(1) Radium together with barium is precipitated upon the addition of a small excess of sulfuric acid Acid soluble substances such as uranium, copper, iron, and phosphate remain dissolved.

(2) Digestion of the radiferous sulfate with a concentrated solution of sodium hydroxide dissolves alkaline soluble

substances such as silica, alumina, lead sulfate, and calcium sulfate. After the residue is washed with water, acid soluble substances are removed by treatment with hydrochloric acid in which radium (and barium) sulfate is insoluble.

(3) Treatment of a radium-containing sulfate with a hot concentrated solution of sodium carbonate converts the sulfate to a radium-containing carbonate. After it is washed, the carbonate is dissolved in hydrochloric acid, and the radium and barium are reprecipitated as sulfates by the addition of sulfuric acid.

(4) The sulfate containing the radium is reduced by ignition at high temperature with charcoal, calcium carbide, calcium hydride, or a mixture of these to an acid soluble sulfide.

(5) The radiferous sulfide is dissolved in hydrochloric acid and the solution treated with hydrogen sulfide to precipitate substances such as lead and copper which form insoluble sulfides. After the hydrogen sulfide is expelled the radium-containing solution is neutralized with ammonia to precipitate the insoluble hydroxides of iron and other metals, such as the rare earths. Radium remains in the filtrate.

In addition to the preceding reactions precipitation of radium nitrate from 80% nitric acid is almost a specific reaction for radium. Only the nitrates of barium, strontium, and lead show a similar insolubility.[34] This chemical property may be used to separate radium from almost all other metal ions; it has been applied to the separation of neutron-irradiated radium from actinium and thorium[29] and to the purification of radium isotopes for radiochemical studies.[20]

Carriers for Radium In addition to barium sulfate and barium chromate (discussed above) other compounds which are good carriers for radium are: ferric hydroxide when precipitated at a moderately high pH with sodium hydroxide, barium chloride (and bromide) when precipitated from a cold mixed solvent of water and alcohol saturated with hydrochloric acid (or hydrobromic acid), barium iodate, and various insoluble phosphates, fluoride, and oxalates (e.g., thorium phosphate, lanthanum fluoride and thorium oxalate).[36]

Barium nitrate precipitated from 80% nitric acid is also a good carrier for radium and has been used to separate radium-223 from its parent and daughter activities.[35]

4. Chelate Complexes of Radium

Radium has the least tendency of all the alkaline earth metals to form complex ions. The formation constants of the radium complexes that have been measured are given in Table III. The complexes are arranged in order of decreasing stability. In every case radium was found to form a 1:1 complex with the complexing agent. The strengths of the various complexes were determined by measuring the distribution of radium between a cation exchange resin such as Dowex 50 and a solution with and without the complexing agent. Also included in Table III are the formation constants for a few barium complexes determined by the same

TABLE III - RADIUM COMPLEXES OF SOME COMPLEXING AGENTS

Complexing Agent	Log K Radium	 Barium	Ionic Strength	Reference
Ethylenediamine-tetraacetic Acid	7.12	7.69	--	61
Nitrilotriacetic Acid	5.75	6.17	--	62
Citric Acid	2.36	2.54	0.16	63
	2.34	--	--	64
Sulfosalicylic Acid	1.9	--	0.16	65
Oxalacetic Acid	1.8	--	0.16	65
Fumaric Acid	1.6	--	0.16	65
Tartaric Acid	1.24	1.67	0.16	63
	1.24	--	--	64
Succinic Acid	1.0	--	0.16	65
Malic Acid	0.95	1.36	0.16	63
Malonic Acid	0.95	--	--	64
Pyruvic Acid	0.89	--	0.16	65
Aspartic Acid	0.86	--	0.16	65

investigators under conditions identical to those used for the radium complexes. Comparison of the constants indicates that barium complexes are stronger than those of radium.

An anion complex of radium, $[RaA]^{-2}$, with the disodium salt of ethylenediaminetetraacetic acid (EDTA) is formed at pH 5.5 to 6.9. No complex forms below pH 4.5, while at pH 7-8 no free radium ions can be detected in solution.[37] An anionic nitrilotriacetate complex, $[RaX]^{-}$, is formed at pH 6-8.[38] The greater stability of the barium complex with EDTA has been used in the fractional separation of barium and radium by ion exchange[39] and by fractional precipitation with HCl after dissolving the mixed sulfates in an ammoniacal solution of the disodium salt of EDTA.[40]

5. Non-Extraction of Radium by Thenoyltrifluoroacetone (TTA) Solutions

No complex of radium with TTA is known. Because of the highly basic character of the radium ion, such a complex could only exist at very high pH. However, extraction from aqueous solution at controlled pH values with a benzene solution of TTA has been used to separate radium from daughter and neutron-irradiation activities including actinium, thorium, polonium, lead, bismuth, and thallium.[41] The radium remains completely in the aqueous phase; all others are extracted into the organic phase at a pH characteristic of the particular element.

6. Extraction of Radium into Organic Solvents

Radium compounds have very low solubilities in organic solvents. One notable exception apparently is the tetraphenylborate which is extractable (90%) at pH 9 by nitrobenzene.[42] Under the same conditions the extraction of francium (cesium and rubidium) is practically quantitative. The presence of EDTA (ethylenediamine-tetraacetic acid) does not affect the extraction of francium but inhibits completely that of radium, thus permitting a separation of the two elements.

As indicated in the preceding section, the insolubility of radium compounds in organic solvents is frequently the basis for the separation of radium from other elements. For example, Häissinsky[43] separated thorium and actinium from radium by treatment of their nitrates with absolute alcohol. The nitrates of thorium and actinium dissolved but not that of radium. Radium has been rapidly freed of its daughter activities (radium D, E, and F) by extraction of their dithizone (diphenyl thiocarbazone) complexes with chloroform.[44] Radium and lead chlorides have been separated by extraction of the lead with a solution of Aliquat 336, a quaternary amine, in benzene; the radium remained in the aqueous phase.[45]

7. Ion Exchange Behavior of Radium

Trace quantities of radium are separated from barium and the other alkaline earth elements by ion exchange.[46,47] Although milligram quantities of radium have also been separated by ion exchange,[48] difficulties result because the radioactivity causes the resin (usually a sulfonated polystyrene crosslinked with divinylbenzene, such as Dowex 50 or Amberlite IR-120) to break down. Insoluble sulfur-containing compounds of radium are produced which are not readily removed from the resin bed.

Cation Exchange Diamond[49] investigated the effect of hydrochloric acid concentration on the distribution coefficient, D, of alkaline earths on Dowex 50. The distribution coefficient was defined as follows:

$$D = \frac{\text{fraction of alkaline earth/gram of resin}}{\text{fraction of alkaline earth/milliliter of solution}}$$

The data are shown in Figure 1. The greater the distribution coefficient the greater the attraction for the resin. Hence,

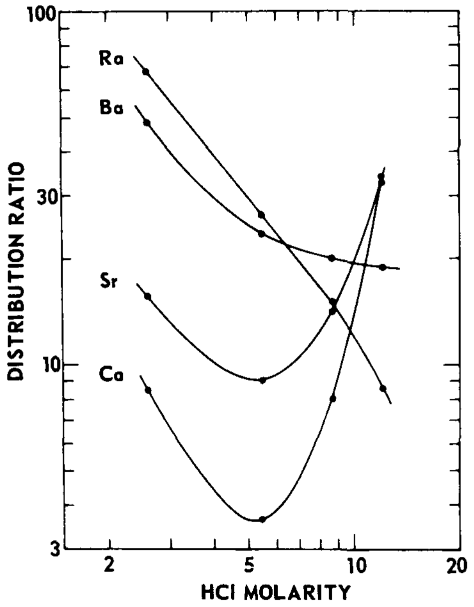


Fig. 1. Variation with concentration of the hydrochloric acid eluant of the distribution ratios of the alkaline earth ions, Ra, Ba, Sr, and Ca on Dowex 50 (10-12% DVB).[49]

in dilute hydrochloric acid, calcium would be eluted from a column first and radium last, but in concentrated hydrochloric acid a reversal of elution order results.

In dilute HCl the order of elution is the same as the order of decreasing hydrated ionic radii, i.e., the largest hydrated ion is bound the least tightly and will be eluted first. Hence, the order is Ca>Sr>Ba>Ra. As the HCl concentration increases, D decreases for all the ions. The decrease for radium is fairly uniform with HCl concentration. Still higher HCl concentrations cause dehydration of the hydrated ions which results in an increase in adsorbability and a minimum in the curves for calcium and strontium at approximately 6M HCl. Although the effect is less for barium, its distribution coefficient is greater than that of radium in 9M HCl. In 12M HCl the order of elution is reversed from that in 3M HCl, i.e., Ra>Ba>Sr>Ca.

Milton and Grummitt[47] separated radium from the alkaline earths and magnesium on a column of Dowex 50 by elution with 1.5M ammonium lactate at pH 7 and at 78°C. A quantitative separation of all the elements from each other was possible in a few hours using 0.25 gram of resin per milliequivalent of sample. A typical elution curve is shown in Figure 2. Ammonium lactate was considerably more efficient than hydrochloric acid as an eluting agent.

Tompkins[46] separated microgram quantities of radium from milligrams of barium and strontium by chromatographic elution on a column of Dowex 50 with 0.5M ammonium citrate solution at pH 7.8. Complete separation was achieved. Radium was eluted from the column after barium and strontium. For the separation of milligram quantities of radium and barium, 0.32M ammonium citrate at pH 5.6 is a more satisfactory eluant from the point of view of both separation coefficient and freedom from precipitation within the column.[48] Mixtures containing over 4000 parts of barium for each of radium were separated with a single elution of the Dowex 50 column.

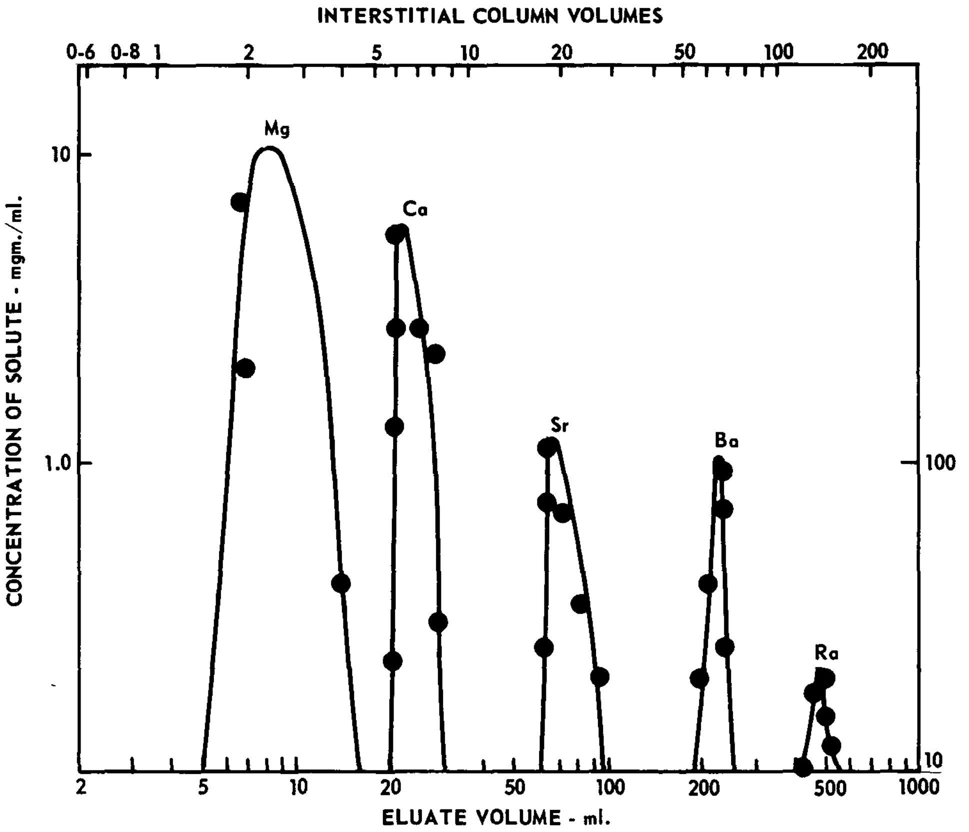


Fig. 2. The separation of magnesium, calcium, strontium, barium, and radium with ammonium lactate eluant--1.5 M at pH 7.1.1X8 cm. column, flow rate 1.0 ml./min., T = 78°C.[47]

Radium has been separated from barium by chromatographic elution (from a column of Dowex 50) with ammonium acetate[50] and EDTA.[51,52] Separation from actinium may be carried out by elution with 70% oxalic acid[53] at 80°C or by elution with mineral acids.[54]

Anion Exchange The absorbability of the alkaline earths on Dowex 1 from an ammonium citrate solution increases in the order Ra<Ba<Sr<Ca.[55] The distribution coefficients decrease with increasing citrate concentration. The same order for the absorbability of the alkaline earths was observed from an

EDTA solution containing ammonium chloride as supporting electrolyte.[56] The stability constant for the EDTA complex of radium was estimated from the anion exchange data to be $10^{7.4}$ which is in agreement with the value reported in Table III.

Because radium does not form a polychloro anion it is not adsorbed from strong hydrochloric acid solutions by Dowex 1. Therefore, it can be separated from those elements which do form polychloro anionic complexes (e.g., uranium, polonium, bismuth, lead, and protactinium) by anion exchange on Dowex 1 from strong solutions of hydrochloric acid. Radium is not absorbed and remains quantitatively in the effluent solution.[57,58]

IV. DISSOLUTION OF RADIUM SAMPLES

Any technique suitable for the dissolution of barium samples[66] will, as a general rule, be applicable to radium.

Radium can sometimes be leached from a solid sample without complete dissolution of the matrix, but quantitative recovery can seldom be assured. However, in the special case of radium adsorbed on soil, e.g., from uranium mill effluents, a relatively mild leaching with dilute (1-2 M) nitric acid will dissolve most of the radium without excessive introduction of interfering elements.

Radium sources fall into three general categories: (1) thorium targets, (2) biological material, and (3) ores. Each type requires special treatment to insure complete recovery of the radium or, in the case of thorium targets, of the intermediate product which decays to a radium isotope.

Thorium metal can be dissolved in either concentrated HCl or concentrated HNO_3, but a small amount of HF or $(NH_4)_2SiF_6$ must be added to prevent formation of a black insoluble residue (with HCl) or passivation (with HNO_3). Hill[67] found that the rate of dissolution of thorium metal is a direct function of the HF concentration, but an excess of HF results in the precipitation of ThF_4. Concentrated HCl containing 0.2 $\underline{M}$ HF is effective in dissolving thorium metal targets; whereas, relatively small amounts of $ThCl_4$ powder can be dissolved in concentrated HCl containing 0.01 $\underline{M}$ HF.

Thorium oxide can be dissolved by prolonged heating with concentrated HNO_3 containing 0.1 $\underline{M}$ $(NH_4)_2SiF_6$.[68]

Soft biological material can be brought into solution by wet-ashing with concentrated or 6$\underline{N}$ HCl or HNO_3, usually in a Kjeldahl flask. Alternatively, it may be decomposed in a muffle furnace, after which the residue is taken up in acid. For the analysis of teeth, all filling materials, carious tissue, stained secondary dentin, and calculus should first be removed. Bone should be boiled in demineralized water to remove excess fat and cleaned thoroughly of any adhering soft tissue before dissolution in hydrochloric acid.[87]

Quantitative recovery of radium from urine can be effected without ashing; addition of ammonium hydroxide to urine precipitates the natural calcium and magnesium phosphates, which quantitatively carry the radium isotopes.[69]

Ore samples usually require vigorous treatment and considerable patience. The procedure used by M. Curie has not been significantly improved upon during the past half century:[102]

> The sample is pulverized and fused with sodium carbonate. The melt is washed with water to remove excess carbonates and with dilute sulfuric acid to remove uranium. The insoluble sulfate residue is fused with sodium carbonate or boiled with a concentrated solution of sodium hydroxide. The soluble sulfates are washed away with water, and the insoluble residue is digested with hydrochloric acid. If the radium is incompletely dissolved, the procedure is repeated.

Rosholt[70] dissolves a sample of one gram or less by first fusing it at almost red heat with four or five grams of sodium peroxide in a nickel crucible. The melt is allowed to disintegrate in water and neutralized with hydrochloric acid.

It is sometimes advantageous to carry out the dissolution in steps aimed at dissolving specific groups of elements rather than the sample as a whole. For example, initial digestion of pitchblende ore with 8N HNO_3 will solubilize all but a relatively small fraction of the sample. The insoluble residue may then be filtered off and fused with sodium carbonate; the relatively small melt is soluble in dilute HNO_3, and the solution may be combined with the main nitric acid filtrate.[71]

Samples containing relatively high proportions of silica may be solubilized by boiling with a mixture of $HClO_4$ and HF. Part of the silica is volatilized as SiF_4, but repeated additions and evaporations with HF may be required to leave a residue which is completely soluble in nitric acid.

Orthophosphoric acid has been used in conjunction with HF to dissolve siliceous minerals.[72] The following procedure is given by Petrow, et al:[58]

> Treat a 1- to 3-gram sample with hydrofluoric and nitric acids, and evaporate dry to eliminate the bulk of the silica. Take up the residue in 5 ml. of hydrofluoric acid and 20 ml. of phosphoric acid. Heat the mixture strongly on a hot plate until dense white fumes appear and then heat in an open oven for 15 minutes or until the mixture forms a clear, viscous liquid. Cool the concentrated phosphoric acid solution slightly and dissolve in 500 ml. of hot distilled water.
>
> Adjust the pH of the solution to 1.0 with a few drops of ammonium hydroxide, and analyze the solution for radium.

Additional procedures will be found in Section VI.

V. COUNTING TECHNIQUES

All radium isotopes decay to either radon or actinium isotopes, all of which are themselves radioactive, and all of which yield radioactive decay products. Consequently, the radiometric determination of a radium isotope must take into account the rapid growth of its decay chain.

The radon daughters present a special problem in that the loss of radon from a radium preparation results in a "disequilibrium" which makes the growth of the subsequent decay products difficult to calculate. Ideally, the radon should be either completely trapped or completely swept out of the radium source, but methods have also been developed for estimating the degree of radon retention in cases where it is either impractical or too time-consuming to eliminate this source of error.[59,74]

Radon retention is a function of sample thickness, and it has been found that ignition at red heat of a carrier-free radium-226 sample mounted on platinum reduced the radon loss to about 30 per cent. Radon loss from an ignited barium sulfate precipitate is negligible, but correction must then be made for self-absorption[75] (Fig. 3 and 11).

For low-level alpha counting of radium sources without loss of radon, Hallden and Harley[76] filter a barium-radium sulfate precipitate on glass fiber or Millipore filter paper, and cover the precipitate with a Mylar film coated with silver-activated zinc sulfide. The scintillations of the phosphor are counted by means of a bare photomultiplier tube connected to an amplification and scaling system.

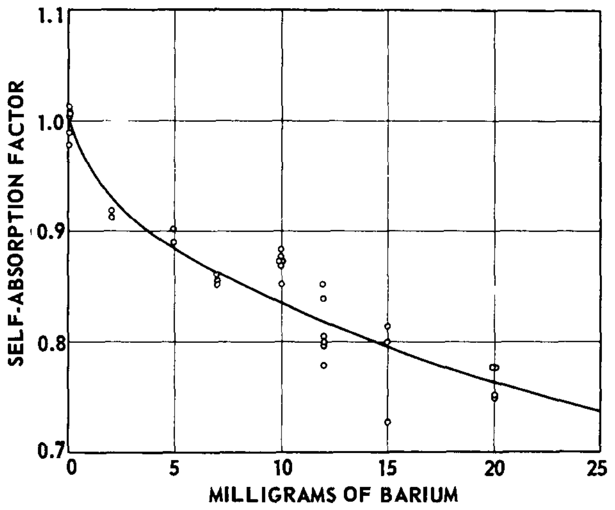


Fig. 3. Absorption of radium alpha particles by barium sulfate deposited over an area of approximately 40 cm².

An interesting technique for alpha scintillation counting of barium sulfate precipitates containing radium is described by Sax and co-workers[80]:

> Transfer weighed precipitate to a plastic Wig-L-Bug vial (Spex Industries, Inc., Hollis 23, New York), Add 100 mg ZnS(Ag). (Type 130, Sylvania Electric Products, Inc., Chemical and Metallurgical Division, Towanda, Pa.),
>
> Using a cardboard shield with a hole in the center so that only the opening of the vial shows through the shield, spray the inside of the vial with

Krylon crystal clear No. 1303 spray coating. The spray can should be held approximately 10 in. from the vial opening,

Add one small plastic bead to the vial (Spex Industries). Quickly snap on cover and place the vial on a Wig-L-Bug amalgamator (obtainable from Crescent Dental Mfg. Co., Chicago, Ill., or from Spex Industries). Set for 2 min. or longer, depending on the amount of precipitate. The mixture of scintillator and precipitate should be completely adhered to the walls of the vial. The vial is placed inside a larger 3-dram plastic vial.

A sketch of the assembled vials is shown in Fig. 4. The foil-covered plug is used to raise the Wig-L-Bug vial above the level of the plastic cap. The aluminum foil disc and aluminum plug covering are used as reflectors.

Cut a No. 1 cork stopper in half. Cover this with foil and glue to the plastic cap. (The glue is made by taking three parts benzene and one part ethylene dichloride and adding enough poly-isobutyl methacrylate to the desired viscosity. The Wheaton vial plastic caps can be obtained from the Packard Instrument Company, LaGrange, Illinois. The aluminum foil is the heavy-duty household type.)

Glue the Wig-L-Bug vial to the foil-covered plug. Then glue the aluminum disc to the top of the Wig-L-Bug vial. Insert the 3-dram plastic vial into a Wheaton vial plastic cap. The rim of the vial should be coated with glue to hold it in place.

A Packard Tri-Carb automatic liquid scintillation spectrometer, model 314X, is used. Dry ice is used for cooling. This eliminates the possibility of random counts being thrown into the system when the compressor goes on or off. Furthermore, the use of dry ice floods the freezer compartment with carbon dioxide gas and reduces the possibility of ambient radon levels in air contributing to background. The instrument settings are as follows:

High voltage: 780 volts
Tap: No. 2
Attenuator: 16
Mode: 4
Discriminators: $5 \rightarrow \infty$
$7 \rightarrow \infty$.

The two discriminator settings are used simultaneously. In this manner, each sample gives two counts simultaneously; and this serves as a check on the instrument. Backgrounds of less than 0.02 cpm are obtained, and a counting efficiency of about 50 per cent is achieved.

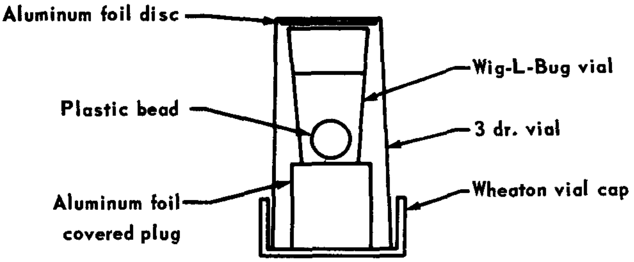


Fig. 4. Assembly of vials for counting.

"De-emanation," the complete removal of radon from a radium source, is practical only with radon-222; the half lives of all other radon isotopes are too short for this technique to be useful. To de-emanate a radium sample, the radium is put into solution and heated gently while a stream of air or an inert gas is bubbled through it. The radon-222 passes out of the solution in the gas stream; and if the bubbling is continued for four or five hours, all of the decay products down to, but not including, lead-210 decay to insignificance. If the radium sample is alpha-counted within one hour after the gas stream has been stopped, the contribution from the decay products will be small, provided that the amount of polonium-210 present is negligible.

On the other hand, the radon-222 swept out of the source may be collected and counted in an ionization chamber; the radium-226 may then be estimated indirectly[78]. This method is particularly useful for the analysis of low-grade ores, since it eliminates the chemical separations which would otherwise be necessary. Several versions of the technique are given in Section VI.

Complete retention of radon can, of course, also be effected by sealing the sample hermetically and beta- or gamma-counting with appropriate correction for counting efficiency. For alpha counting, the source is sealed with a thin mica window.

In determining the specific activity of radium-226, Sebaoun[77] prepared thin films of radium chloride on platinum as follows:

> The source support is a platinum disk 25.4 mm. in diameter and 0.1 mm. thick, perfectly flat and

polished. The support is boiled in concentrated HNO_3, rinsed with distilled water and acetone, and finally brought to red heat for several minutes in a flame. A thin line of varnish is drawn, forming a circle 12 mm. in diameter and well centered.

With the aid of a calibrated micropipet, 50-70 λ of the radium chloride solution is deposited inside the ring, and a drop of tetraethylene glycol is added. With the point of a fine glass rod, the mixture is homogenized. The quantity of TEG is not critical; the same results were obtained with volumes of TEG ranging from 10 to 20 λ.

The source is dried with the aid of an infrared lamp placed 30 cm. above the plate. The varnish ring prevents the TEG from spreading as the water evaporates. The evaporation must be carried out slowly, precautions being taken to avoid the formation of bubbles. When the water is evaporated, the lamp is lowered gradually to 20 cm. above the plate. Under the action of heat, the TEG undergoes a partial polymerization, and a finely divided precipitate of $RaCl_2$ is formed. When the preparation is completely dry, the platinum disk is brought to red heat with a Meker burner to eliminate the last traces of organic matter. An

> adherent film of $RaCl_2$ remains, which is distributed in a very uniform manner.
>
> The source is covered with a thin sheet of mica, transparent to alpha particles. The mica, which serves to prevent the loss of radon, is applied as follows:
>
> A thin layer of araldite (an epoxy resin which hardens in the cold) is spread on the platinum, without solvent, to within 2 mm. of the $RaCl_2$ film, and the dust-free strip of mica (25 mm. in diameter) is placed on top. Once the araldite has polymerized, a second layer 0.2 mm. thick is applied on top of the mica, to within 1 mm. of the edge of the first layer.
>
> The thickness of mica ranged from 1.26 to 1.48 mg/cm^2.

The decay products of radium-223 grow so rapidly that it is usually more convenient to allow the six hours necessary for equilibrium than to attempt to correct for partial equilibrium. Radium-224, however, does not attain equilibrium until five or six days after its separation from lead-212. Since the radium-224 half life is only 3.64 days, it is usually preferable to wait only 10 hours, or overnight, and to correct for lead-212 disequilibrium. Tables are available for facilitating such corrections[79].

Radium-228 separated from thorium-232 is always contaminated by radium-224 and its beta-emitting decay products. However, actinium-228, the 6.13-hour daughter of radium-228, can be rapidly separated from the radium isotopes by a variety of techniques (See Section VI) and is useful in the indirect radioassay of radium-228.

Gamma-counting and gamma spectrometric methods are rapid and non-destructive, but are reliable for quantitative radioassays only to the extent that satisfactory standards are available for the determination of counter efficiency. Standard samples of radium-226 are available from the National Bureau of Standards, but all other radium isotopes must be specially prepared and standardized by absolute counting methods. The gamma spectrum of radium-226 is shown in Fig. 5.

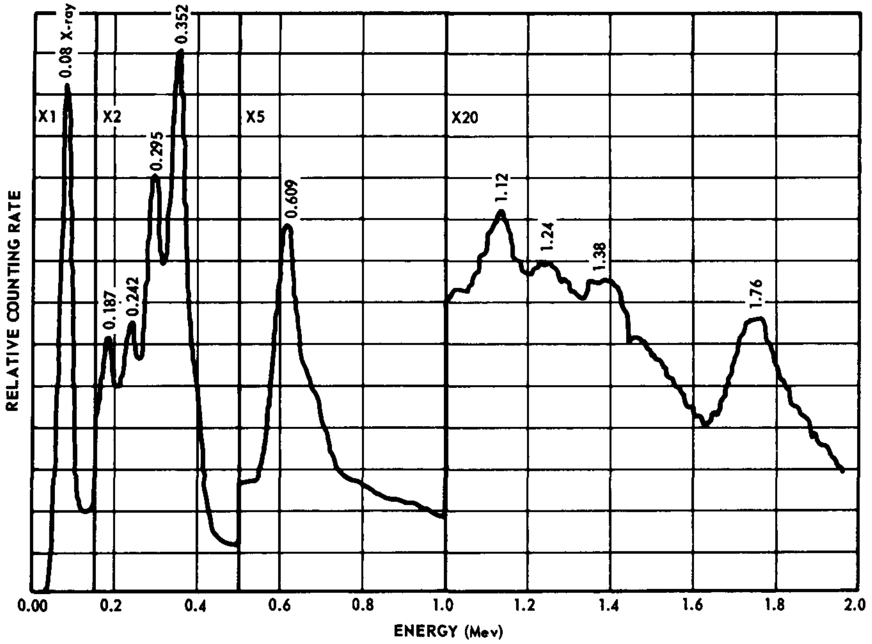


Fig. 5. Gamma spectrum of radium-226 and daughters.

The most convenient radium isotope for use as a gamma-emitting tracer is radium-223 because of its relatively long half life (11.435 days), the rapid attainment of equilibrium by its daughter products, and the ease with which it can be separated in carrier-free form from its long-lived parent, actinium-227. The gamma spectrum of radium-223 is shown in Fig. 6a.

The gamma spectrum of an equilibrium sample of radium-224 is virtually indistinguishable from that of its parent, thorium-228. The only difference is in the energies of the Kα X-rays accompanying the alpha disintegrations; 0.0838 and 0.0885 mev., respectively.[113] Gamma spectroscopy is not, therefore, a useful method for following the separation of radium-224 from thorium-228. For reference purposes, however, a gamma spectrum of radium-224 is shown in Figure 6b.

The rapid development of solid state alpha detectors has inspired an increasingly wide use of alpha spectrometry for the analysis of mixtures of isotopes, including radium isotopes. Nevertheless, alpha spectrometry, whether by solid state detectors, gridded chambers, or absorbers, imposes severe restrictions on the method of sample preparations. The most important of these are sample thickness and area.

It is essential that samples prepared for solid state alpha spectrometry be thin enough so that there is no significant attenuation of the alpha particles within the source itself. Furthermore, the area covered by the active deposit should be small so that all particles counted arrive at the detector at

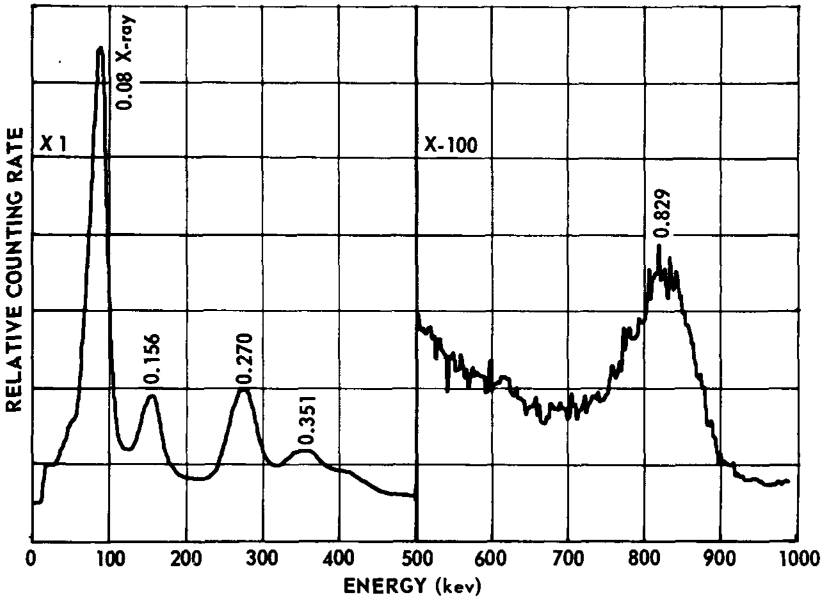


Fig. 6a. Gamma spectrum of radium-223 and daughters.

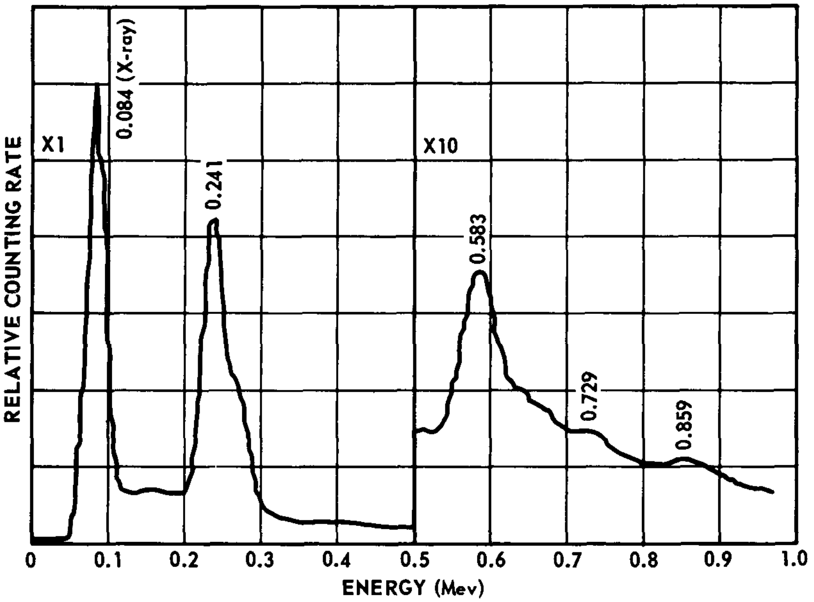


Fig. 6b. Gamma spectrum of radium-224 and daughters.

an angle normal to the surface. This latter requirement can be achieved, if necessary, by collimation or by low geometry counting. The requirement of sample thinness is somewhat more difficult.

The method of Sebaoun[77], cited above, can be used if the mica window is eliminated, but the danger of detector contamination by radon isotopes and their decay products is increased. Asaro, et al.[81] prepared a source of radium-224 as follows:

> A dilute acid solution of Th^{228} was fed to a Dowex-50 cation exchange resin column upon which the Th^{228} and most decay products were adsorbed. Upon passing 4M HNO_3 through the column, the thorium fraction remained and the radium washed through. The radium fraction was concentrated and then evaporated to dryness on a tungsten filament which could function as a heater.
> By heating the filament at dull red heat, any polonium present was removed, as was the lead (ThB). The temperature was raised, and the radium-224 was sublimed in vacuum onto a platinum plate, masked to approximate a line source of alpha activity.

Another useful method for the preparation of thin sources of radium or other radioelements is the following:[82]

> Mask all but a small central area of a platinum disk by spraying it with Krylon Crystal Clear Spray Coating, or by applying collodion or Zapon lacquer with a camel's hair brush. Allow the mask to dry in air. Deposit a dilute solution of HNO_3 containing the radioisotopes in the unmasked area and evaporate to dryness on a hot

plate at a temperature between 90° and 100°C. Cover the dried area with 0.1 N HNO_3 and add one drop of concentrated NH_4OH. Evaporate the solution to dryness. Slowly raise the temperature until the residual NH_4NO_3 has been sublimed. Heat the plate to red heat to burn off the organic matter. The active deposit remains as a uniform and adherent thin coating.

VI. DETAILED RADIOCHEMICAL PROCEDURES FOR RADIUM

Reviewer's Note

Considerable attention has been given to the development of procedures for determining radium in biological samples, especially human urine. The maximum permissible amount of radium-226 permanently fixed in the body is 0.1 microgram, and only 0.01 to 0.0005 per cent of the body radium is excreted daily in urine.

Consequently, analyses must be made for concentrations of radium as low as one picogram per liter.

Many of the health physics procedures are directly applicable, or easily adaptable, to the radiochemical analysis of inorganic sources, such as minerals, sea water, and process effluents. They should, therefore, not be ignored by the inorganic radiochemist, particularly if the quantities of radium sought are small.

Procedure 1

Sampling and Determination of Radon[83]

Principle

When radium is present in the body, the gaseous daughter product radon, ($T_{\frac{1}{2}}$ = 3.8 d), will collect in the lungs and will be eliminated with each exhaled breath.

One liter glass sampling flasks are provided for the purpose of collecting breath or atmospheric radon samples.

The radon sample is transferred to a pulse type ionization chamber, and after it is allowed to come into equilibrium with its daughter products, the sample is alpha counted. Two of the daughters, Po^{218} (RaA) and Po^{214} (RaC'), are alpha emitters and contribute to the total count.

Special Apparatus

a. Sampling

1. One liter glass flasks with two large bore stopcocks per flask.

2. Tank of compressed, aged air with two stage regulator.
3. Face mask (Mine Safety Appliance Co. #CS 6772 inhalator modified to block emergency intake and outlet modified to adapt 3/8" tubing).
4. Demand Regulator (Mine Safety Appliance Co. #CS 46516 single stage or equivalent).

b. Sample Analysis

1. Platinum black catalyst
2. Drying tube with Drierite.
3. Flame arresters.
4. Capillary orifice.
5. Vacuum pump.
6. Copper tube (½" x 5") sealed at one end, brass fitting at the opposite end.
7. Tank of hydrogen with two stage regulator.
8. Tank of forming gas (85% N_2, 15% H_2) with two stage regulator.
9. Sample introduction system including valves and piping.
10. Pulse type ionization chamber and associated electronic equipment.

A. Sampling Procedure

a. Breath Radon

1. Set up the equipment using 3/8" (9.5 mm.) rubber tubing on the inhalator outlet. Do not attach to sampling flask.

2 Clean facepiece with cotton and alcohol.

3. Set air pressure on two-stage regulator to 10 lb. (4.5 kg).

4. Have the subject hold the facepiece in place while you check for leaks, particularly around the bridge of the nose

5. Have the subject breathe with the respirator for five minutes to flush the environmental air from his lungs. (This should be regular breathing. Do not ask for deep breaths.)

6. While the subject continues breathing as before, attach the sampling flask (with both stopcocks open) for a one-minute period, remove and close stopcocks.

b. Atmospheric Radon

1. Open both flask stopcocks.

2. Connect 2 ft. of 3/8" rubber tubing to one stopcock.

3. Inhale through tubing 20 times. Do not exhale through flask. If convenient, a suction pump may be used.

4. Close both stopcocks.

B. Sample Preparation

a. All Sample Types.

1. Connect sample flask to hydrogen tank with rubber tubing.

2. Raise gage pressure to 8 pounds per square inch.

3. Open flask stopcock to tank to admit hydrogen.

4. Close stopcock and tank valve.

C. Counting Procedure

1. Raise forming gas line pressure to 7 psi and bleed line.
2. Connect one flask stopcock to forming gas line (N_2+H_2) with rubber tubing, the other to the counting system.
3. Open ionization chamber and vacuum line valve to evacuate counting chamber, external piping and rubber hose to flask.
4. Close vacuum line valve when system reaches minus 30 in. of mercury gage pressure (0.00005 mm. Hg).
5. Open flask stopcock to counting system. Allow pressure equilibration (indicated by pressure gage).
6. Check platinum catalyst by touch to assure that combination of H_2 and O_2 is occurring.
7. Open stopcock to forming gas line. Allow forming gas to flush through flask until system pressure reaches 7 psi.
8. Close all valves and remove flask and hoses from system.
9. Turn on ionization chamber voltage.
10. Count the sample for at least 14 hours.

D. Calculations

1. Discard first 2 hours of counting data (equilibration of radon and daughters).
2. Determine gross count over remaining counting period.
3. Calculate net counts per hour per sample by determining gross sample counts per hour and subtracting background counts per hour.

4. Divide net counts per hour by the chamber standardization value of net counts per hour per micro-microcurie of radon of sample.
5. Using the midpoint of the counting interval as the time of counting, extrapolate the value obtained to the time of sampling.

E. Notes

Tolerance Levels for Radon

The accepted maximum permissible level of radon in breath is 1×10^{-12} curies/liter. This is the amount of radon in equilibrium with 0.1 μgm of fixed body radium. Unexposed persons indicate a normal breath radon concentration of about 6×10^{-14} curies/liter.

For extended periods of breathing of contaminated air, the accepted maximum permissible level of environmental radon and its daughters is 1×10^{-10} curies/liter.

Background

The background on the radon chambers is run with forming gas as the filling gas. Background is run for at least 14 hours on each chamber.

Flame Arresters

The removal of oxygen from the sample takes place in the platinum black catalyst where oxygen and hydrogen combine to form water. This combustion reaction generates a considerable amount of heat; and if allowed to strike back, the sample may explode. In order to prevent such explosions, flame arresters are placed before the catalyst. The flame arresters consist of a fine mesh copper wire screen and act to dissipate the heat of the reaction.

Capillary Orifice

A capillary orifice is placed in the line after the catalyst. This slows passage of gas through the catalyst and insures complete combustion.

Sample Preparation

Before transfer to the counting system, enough hydrogen is added to the sample flask to completely remove oxygen (as H_2O) in the platinum catalyst. Because oxygen acts to quench the ionization produced by each alpha disintegration, even small amounts of it in the chamber will seriously affect the counting rate of a sample. Environmental air contains about 20% oxygen; and therefore, the addition of 6 psi of hydrogen is sufficient for all samples. It has been our practice to add an excess of hydrogen and, therefore, 8 psi is usually added to each sample.

Counting Apparatus

The radon counting apparatus consists of a sample introduction system, ionization chamber, preamplifier, amplifier, and mechanical registering device. The ionization chamber counts each alpha disintegration of radon and about 50% of the disintegrations of its daughter products. Each chamber plus its sample introduction system has a capacity of two liters and the chamber is operated at a potential of 1000 volts. A mixture of hydrogen (15%) and nitrogen (85%) is used as a counting gas. The chambers are constructed of a specially selected, electropolished, stainless steel and have a background count of about 10 counts per hour. A block diagram of the counting system and external apparatus is shown below.

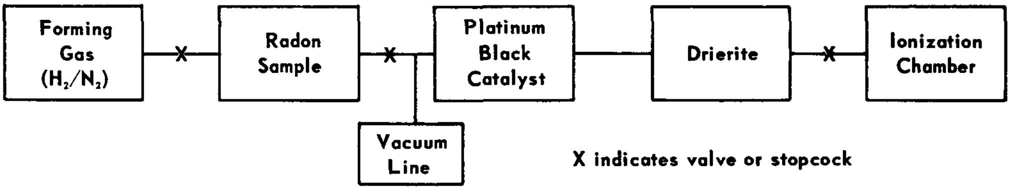


Fig. 7.

Standardization

Each unit is standardized with radon from a radium solution containing 10^{-12} gm of radium. The standard radium solution is obtained from the National Bureau of Standards and is diluted and split into aliquots which are sealed in small glass ampoules. The radon is allowed to build up for a minimum of 30 days before the standard is used.

The standard is transferred to a copper tube and a plug of Pyrex glass wool inserted. The tube is then attached to the external feed system. When the ionization chamber and external system are evacuated, the vacuum line is shut off from the system and the copper tube crushed with a pair of pliers until the standard tube cracks. The copper tube is then heated sufficiently to drive off the radon from solution. Forming gas is introduced to flush the radon into the chamber and the system is brought to a pressure of 7 psi.

At equilibrium, there are three alpha disintegrations per radon disintegration; however, two of these are from the particulate alpha emitting daughters and since these deposit on the walls of the ionization chamber, they are counted with a maximum efficiency of 50%. One micro-microcurie of radon in the ionization chamber thus has a theoretical counting rate of 266 counts/hour. Actually, the ionization chambers in this laboratory yield a counting rate of 220 counts/hour per micro-microcurie of radon in equilibrium with its daughters or an efficiency of 83%.

To check the chamber during servicing, a plated uranium source may be placed in the base of the chamber through a plug. The efficiency of the chamber under these conditions is 50%.

Reviewer's Note

This procedure, with minor modifications, can be applied directly to the analysis of radium-bearing minerals. Standard rock samples can be obtained from the National Bureau of Standards.

Procedure 2

Emanation Method for Determination of Radium[85]

Procedure

The amount of solution used is 100 to 200 ml, containing roughly 10^{-9} g of radium. If necessary, however, solutions containing as much as 10^{-8} g of radium or as little as 10^{-13} g can be measured.

The solution is placed in flask S (see Fig. 8), fitted with a reflux condenser, and de-emanated by boiling at a reduced pressure of approximately 0.5 atm, while nitrogen is bubbled through it, usually for 17 or 18 min. The flask is then sealed off by stopcocks T_1 and T_2, at atmospheric pressure, and the radon is allowed to collect until it is transferred to the chamber. The usual collection time that is convenient is of the order of one day. The amount of radon in curies collected is equal to $(1-e^{-\lambda t})M_{Ra}$, where M_{Ra} is the amount of radium in solution in grams, t is the time of collection in hours, and $\lambda = 0.00755$. The longer the collection time (up to a practical limit of about 30 days), the more radon is collected per gram of radium. In measuring small quantities a longer collection time would be an advantage.

The transfer of the radon is accomplished by reboiling in the same manner as above and allowing the nitrogen containing the radon to flow into the evacuated ion chamber. The nitrogen is purified by passing through hot reduced copper, C, to remove oxygen; through Drierite (B_1) and P_2O_5 (B_2) to remove water vapor; and through Ascarite (B_1) to remove CO_2. The radon is allowed to come to equilibrium in the chamber for at least 3 hours. The count is usually made for 12 hours during the night, when vibrations and voltage fluctuations of power lines are less prominent.

The calculations consist in determining the average count per hour above background and dividing by $K(1-e^{-\lambda t})e^{-\lambda T}$, where K is the calibration count per hour per curie, determined by running a standard radium solution containing 10^{-9} g of radium; $\lambda = 0.00755$ per hour; t is the collection time in hours; and T is the decay time in hours, which is the interval between the transfer of the radon to the chamber and the beginning of the 12-hour record. If the calibration count is made for the same period, in this instance 12 hours, no additional correction is necessary.

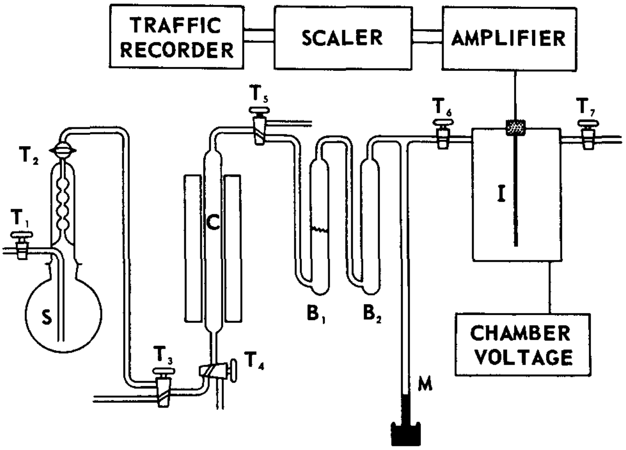


Fig. 8. Schematic diagram showing separation and determination of radon. S, standard radium solution; C, reduced copper; B_1, Drierite; B_2, P_2O_5; M, open mercury manometer; I, ion-counting chamber; T_1 to T_7, stopcocks.

Procedure 3

Emanation Method for Radium Analysis[78]

Principle

Radon-222 is flushed out of a radium-containing solution and counted to estimate the amount of radium present.

Apparatus

The emanation apparatus (Fig. 9) consists of a 250-ml boiling flask, A; water-cooled reflux condenser, B; cold trap, C; mercury manometer, D; spray filter, E; and connections at M, F, and K for vacuum pump, ionization chamber, and argon tank, respectively. An important feature for routine measurements is the interchangeability of boiling flasks and ionization chambers. The ionization chambers are not permanently attached either to the emanation line or to the electrical circuit but can be connected to either at will. This provides an economy of apparatus, for only one emanation line and one counting circuit are necessary, and neither need be held up by a single sample longer than the time of actual use. It also provides a flexibility of operation, which is convenient when samples cover a wide range of concentrations.

An emanation flask can be sealed when off the line by means of an interchangeable connecting section, H, containing a 6-mm-bore stopcock and standard-taper ground-glass joints fitting the flasks and the condensers. The flask, A, and the connecting sections, H, are held together by means of rubber bands fitting over the female portion of the stopcock and ears projecting from

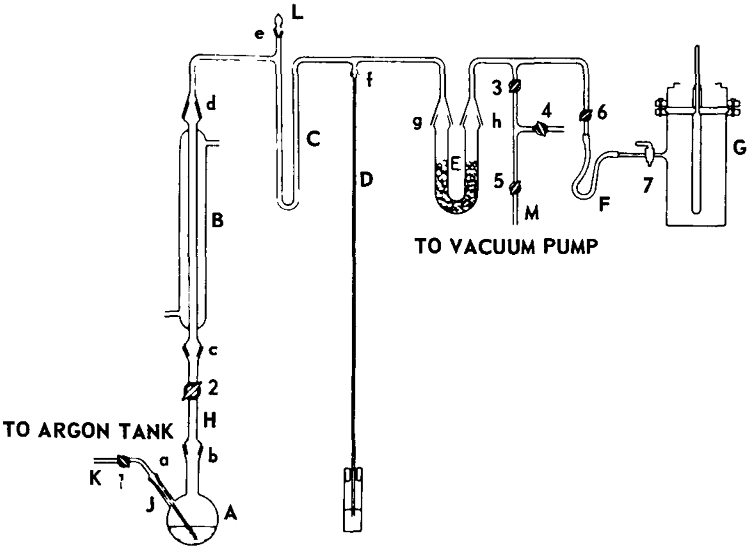


Fig. 9. Emanation apparatus.

a metal collar fastened to the flask. Each flask is provided with a side arm, J, into which fits a gas-inlet tube, K, also equipped with a stopcock. The manometer is made of 1-mm-bore capillary tubing to minimize loss of activity. The male joint at f is made by grinding the tube to fit into a standard-taper female joint. Apiezon N grease (Metropolitan-Vickers Electrical Co., Ltd.) is a satisfactory lubricant for stopcocks 3, 4, 5, 6, and 7 and joints d, e, f, g, and h. Cello-Grease (Fisher Scientific Co.) is a good lubricant when high temperatures are involved, as for stopcocks 1 and 2 and joints a, b, and c.
The ionization-chamber design developed after experimentation with several types is illustrated in Fig. 10; it represents a considerable simplification over that of Curtiss and Davis.[85] By applying the high potential to the center electrode and grounding the other cylinder, the need for an additional

shielding cylinder is eliminated. By supporting the collecting electrode in the middle of the large insulating plate (Lucite) that forms the top of the chamber, it becomes unnecessary to use a guard ring, and consequently there is no dead space in the chamber. A further disadvantage of a guard ring is that it collects electrons produced in the top of the chamber and thus reduces the size of some of the pulses.

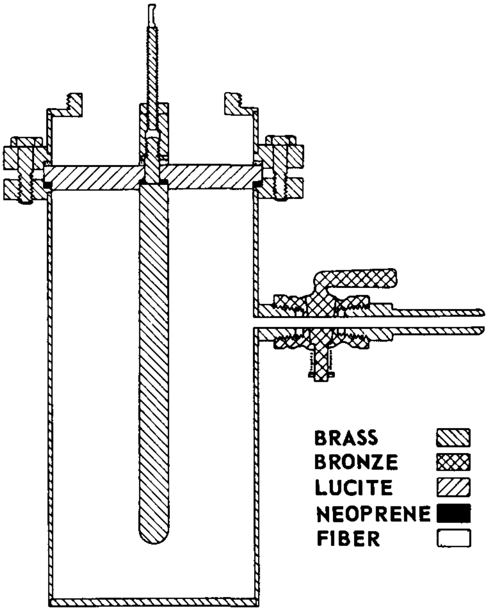


Fig. 10. Ionization chamber.

The chamber fits into the breech-locking receptacle of the Metallurgical Laboratory Instrument Section standard α counter by means of the breech thread on the cap. The banana plug on the end of the adjustable extension makes contact with the high-voltage and amplifier circuit as explained below. The valve is a commercial steam cock, No. 1037 bronze-spring key type with double female 1/4-in. I.P. ends and lever handle, obtained from the Lunkenheimer Co., in which the tightness is maintained by means of a spring. Apiezon N is a satisfactory stopcock lubricant. Neoprene gaskets are used for the gastight seals, and fiber washers are used to protect the outside of the Lucite insulator from direct contact with metallic surfaces. Four bolts, evenly spaced aroung the top, hold the chamber together with sufficient pressure on the baskets.

The body of the chamber is made of brass, silver-soldered together. Backgrounds, after careful cleaning, are 4 to 10 counts per minute. Painting the inside surface with several coats of silver paint, obtained from the Electrochemicals Dept. of E. I. du Pont de Numours & Co., reduces the backgrounds to approximately 2 counts per minute. Reducing the background is important because the lower limit of detection of radon varies with the square root of the background.

Preparation of Samples for Radium Assay For radium assay by the emanation technique, the radium must be completely and quantitatively dissolved. It is desirable that all the radium of a sample be obtained in a single solution. The volume of solution to be emanated must be not over 125 ml, and it must not contain nitric or hydrochloric acid in concentration greater than 2$\underline{N}$ when diluted to this volume. If possible, the sample size should be such as to yield, after a convenient growth period, a counting rate between 1,000 and 10,000 per minute, preferably in the range of 3,000 to 5,000 counts per minute. A sample containing 10^{-8} g Ra will give roughly 5,000 counts per minute after an overnight growth period. The approximate counting rate can be adjusted by varying the size of the aliquot and the time of growth.

Radium Standards U. S. Bureau of Standards radium-solution capsules are opened by filing and breaking the constricted end. The contents are then made up to a known volume in a volumetric flask. Suitable aliquots are taken for measurements and diluted to approximately 100 ml with 1$\underline{N}$ HCl.

Process Solutions These present no difficulty since a measured volume of a solution can be introduced directly into an emanation flask and diluted, if necessary, to about 100 ml. Certain process filtrates contain lead sulfate, which slowly precipitates on cooling and standing. On heating, the precipitates redissolve, so that these samples can be analyzed without additional treatment.

Pitchblende Ores A 0.1-g sample is weighed into a 50-ml platinum dish and treated with 15 ml of 2$\underline{N}$ HNO_3 on a hot plate. When the reaction subsides, 10 to 20 ml of concentrated nitric acid is added, and heating is continued for 1/2 hr Ten milliliters of 40 per cent HF and 0.5 ml of 70 per cent $HClO_4$ are added, and heating is continued until perchloric acid fumes are given off. Additional hydrofluoric acid and nitric acid are added and the dish is again heated until perchloric acid fumes appear. This is repeated once or twice more. Twenty-five milliliters of 6N HNO_3 is added; the solution is heated until clear and is transferred to an emanation flask, using 75 to 100 ml of water to wash the sample quantitatively into the flask.

Gangue-Lead Sulfate Cakes The material is dried and ground for analysis. A 0.1- to 0.2-g sample is weighed into a No. 00 porcelain crucible and intimately mixed with ten times its weight of zinc dust. The crucible is covered and heated in a Meker flame for 1 hr After cooling, the crucible and cover are placed in a 250-ml beaker and covered with 2N HNO_3. When the reaction subsides, the beaker is heated on a hot plate until the zinc is completely dissolved. The crucible and cover are then removed and washed with water, and the solution is evaporated to about 50 ml and filtered quantitatively. The filter paper with the insoluble residue is transferred to a platinum crucible, and the paper is burned off. The residue is evaporated to dryness twice with 10 ml of hydrofluoric acid. Concentrated nitric acid is added to dissolve the material remaining, and the solution is added to the filtrate obtained previously. The solution is then evaporated to a convenient volume for analysis.

Barium Sulfate Cakes The material is dried and ground for analysis. A 0.3- to 0.4-g sample is weighed into a No. 00 porcelain crucible and treated in the manner described for gangue-lead sulfate samples. After treating the filter-paper residue with hydrofluoric acid, some undissolved barium sulfate remains. This is transferred to a porcelain crucible with water and a rubber policeman, evaporated to dryness, and treated with zinc as before. The sinter dissolves completely in nitric acid. The two solutions are then combined and evaporated to a convenient volume for analysis.

Emanation Procedure

The radium-containing sample, in 75 to 125 ml of solution, is placed in a flask and attached to the line. The cooling bath, a mixture of dry ice and n- butyl alcohol in a Dewar flask, is placed around the cold trap. The gas-inlet tube is attached to the argon tank with a rubber tube. The system is then opened to the vacuum pump via stopcocks 3 and 5 with stopcocks 1, 2, 4, and 6 closed. After the system has been evacuated, stopcocks 1 and 2 are opened simultaneously, and a slow stream of argon is allowed to enter through stopcock 1 until the mercury column is depressed to 20 to 30 cm. This regulation is achieved readily by integrating the manipulation of stopcocks 1 and 5. The solution is boiled gently for 20 min with a small gas burner. At the end of this time the flame is removed, stopcocks 3 and 5 are closed, and the time at which boiling is discontinued is noted. The argon is allowed to continue to flow until atmospheric pressure is reached. Stopcocks 1 and 2 are closed, and an ice bath is raised around flask A to effect rapid cooling of the solution to room temperature. The system is again brought to atmospheric pressure by opening stopcock 2 and allowing argon to flow through stopcock 1 until this condition is attained. The cooling and the pressure adjustment are accomplished in less than 5 min. Stopcocks 1 and 2 are closed, and the flask is removed from the line. This process flushes the solution and flask of air and radon. It is necessary to adjust the pressure to near atmospheric with the flask at room temperature, otherwise, the pressure differential may cause air to leak in or radon to leak out during the storage period. The flask is stored on a suitable rack until sufficient radon for measurement has accumulated, usually overnight or longer.

In order to measure the radon the aged flask is again attached to the line, and an ionization chamber, G, is attached to outlet F by a short rubber tube, as shown. The chamber and line down to stopcock 2 are pumped out, filled with argon through stopcock 4, and pumped out again. This flushing process is carried out several times Stopcocks 3, 4, and 5 are closed when the system is left evacuated as a result of the final flushing. Stopcock 2 is opened, and the emanation is driven off into the chamber with a slow stream of argon through stopcock 1, the flow rate being adjusted to bring the pressure to atmospheric in 20 min and the solution gently boiled with a small burner as before. The time at which boiling is discontinued is noted. The flask may now be stored for another radon-accumulation period. The chamber is removed for counting.

From time to time it is necessary to remove the water that has accumulated in the cold trap. This is done with a long, thin-stemmed pipet after removing the ground-glass stopper L.

After the chamber has been counted, it is evacuated and filled several times with argon and allowed to remain evacuated overnight so that the active deposit may decay completely. Before reusing the chamber, it is flushed several times with argon and its background measured. For this flushing process the line is not used; instead, only the chamber is evacuated and filled with argon directly from the tank.

Argon is used as the ionization-chamber gas because of its desirable characteristics for α-particle counting. It is a free-electron gas, yielding sharp, fast pulses at low collecting potentials. Argon gives a relatively large number of ions per unit of energy expended. Its relatively high atomic weight results in short α tracks, which reduce the probability of striking a wall before producing sufficient ionization to count. It is readily available in a sufficiently pure state, 99.6 per cent commercial tank argon being highly satisfactory. Sufficiently pure tank nitrogen would be almost as good for this purpose.

For health reasons, i.e., to prevent air contamination by radon, it is advisable to place the vacuum pump in a hood.

The line is checked periodically for contamination by using a flask containing pure water and following the procedure as described above for radium samples.

The spray filter, containing glass wool, was found to be necessary when samples containing extreme amounts of α activity were tested for radium. For small amounts of radium it may be omitted from the line, but its use is desirable as a precautionary measure.

(Reviewer's note: The ionization chamber can be replaced by an alpha-scintillating radon counter bottle, available from W. H. Johnston Counter Laboratory, 3617 Woodland Avenue, Baltimore 15, Md. This zinc sulfide-coated container is filled with radon, placed on the end of a photomultiplier tube, and covered with a light shield. When the high voltage is turned on, the alpha particles are counted with an efficiency that permits routine measurements of radon-222 concentrations as low as 0.01 picocurie.[115])

Procedure 4

Indirect Determination of Radium-224 in Urine[83]

Principle

The radium-224 content of urine is determined by chemical isolation of lead-212 and radiometric assay of bismuth-212 and polonium-212 after equilibration. Pb^{212} and the isotopes of radium, thorium, and actinium are collected from untreated urine by coprecipitation with calcium phosphate. Thorium, actinium, and calcium are then removed by coprecipitation of lead with barium nitrate in the presence of lanthanum hold-back carrier. Radium and added barium are removed by selective precipitation of barium chromate in the presence of ethylenediaminetetraacetic acid. Lead in the filtrate is released from the chelate by the addition of nickel and is finally collected as lead chromate.

The lead precipitate is stored to allow the equilibration of Bi^{212} and Po^{212} with Pb^{212}. The resulting alpha activity is then determined by covering the precipitate with a silver activated zinc sulfide film and measuring the photo-emission with a bare phototube. Instrument response is converted to the alpha disintegration rate by application of corrections for counter efficiency and background, self-absorption and recovery. Precision is expressed as one standard deviation due to counting error. The Ra^{224} disintegration rate is calculated from the combined alpha activity of Bi^{212} and Po^{212} by application of the Bateman function for the decay of the thorium series.

Special Reagents

1. Lead carrier solution - 7.99 g $Pb(NO_3)_2$/1. in 1% HCl.
2. Barium carrier solution - 7.58 g $BaCl_2$/1.
3. Lanthanum carrier solution - 31.2 g $La(NO_3)_3$/1. in 1% HCl.
4. Sodium chromate solution - 0.5<u>M</u> Na_2CrO_4.
5. Nickel chloride solution - 110.0 g $NiCl_2$/1. in 1% HCl.
6. EDTA solution - 100.0 g (tetrasodium salt) ethylenediaminetetraacetic acid/1.H_2O.

Sample Preparation

1. Transfer a measured volume of urine to a 250 ml. centrifuge bottle.
2. To the sample add 2 ml. of H_3PO_4. Adjust the pH to 9 with NH_4OH. Stir, centrifuge, and discard supernate.
3. Dissolve the precipitate with 10 ml. of HNO_3. Dilute to about 100 ml. with H_2O. Repeat step 2.
4. Dissolve the precipitate with 10 ml. of HNO_3, and transfer to a 100 ml. beaker. Evaporate to near dryness. Repeat the evaporation with 10 ml. aliquots of HNO_3 until the solution is clear.
5. Dilute the sample to about 5 ml. with H_2O. Add 1 ml. each of barium, lead, and lanthanum carrier solutions.
6. Add 50 ml. of 90% HNO_3. Stir for 20 minutes, cool, and filter over glass fiber filter paper. Discard the filtrate.

7. Dissolve the precipitate from the filter with H_2O. Collect the solution in a 100 ml. beaker. Evaporate to about 5 ml. and repeat step 6.

Determination

1. Dissolve the precipitate from step 7, Sample Preparation, from the filter with H_2O. Collect the solution in a 40 ml. centrifuge tube.
2. Add 3 ml. of glacial acetic acid. Adjust the pH to 5.5 with NH_4OH. Add 1 ml. of sodium chromate solution with stirring. Cool, centrifuge, and discard the supernate.
3. Dissolve the precipitate with 5 ml. of 1N HCl. Dilute to 20 ml. with H_2O. Add 1 ml. of EDTA solution and 3 ml. of glacial acetic acid.
4. Adjust the pH to 5.5 with NH_4OH. Heat in a water bath to 95°C. Add 1 ml. of sodium chromate solution with stirring. Cool, centrifuge, and decant the supernate into a 40 ml. centrifuge tube. Discard the precipitate.

5. To the supernate add 1 ml. of nickel chloride solution. Heat to 95°C in a water bath with stirring. Cool, and filter over a weighed glass fiber filter paper. Wash with H_2O.
6. Dry the precipitate at 100°C. Weigh and mount under a zinc sulfide phosphor disc. Store for ten hours and alpha count.

Alpha Phosphor on Mylar[76]

The phosphor is the standard silver-activated zinc sulfide (Sylvania Type 130 [P-7] or duPont 1101 phosphor) coated on one side of a Mylar film. The material is spread using the zinc sulfide as a pigment in a modified alkyl vehicle.

A fresh die-cut phosphor disc, 15/16 inch in diameter, is used for each sample. The sample filter paper is laid on a nylon disc, the phosphor is placed against the sample, a strip of 0.0005-inch Mylar is overlaid, and the assembly is locked together with a nylon ring.

Counting is performed with a bare phototube on either manual or automatic counters. Any phototube system may be modified to use this technique.

The phosphor is available as Type AST-3 phosphor from William B Johnson & Assoc., Inc., P. O. Box 415, Mountain Lakes, New Jersey
The approximate prices are:

Strips: (minimum order 10 foot lengths)
13" width $3.00 per linear ft.
6" width $2.00 per linear ft.
2" width $1.00 per linear ft.
Discs: (Circles)
15/16" $15.00 per 1000
2" $25.00 per 1000
Other sizes and shapes - price on request.

Calculations

The Bi^{212}-Po^{212} disintegration rate is obtained from the net counting rate of the lead chromate precipitate through the following calculation:

$$d/m = R_s YTE$$

where R_s is the net counting rate of the sample, Y is the recovery factor, T is the precipitate thickness correction, and E is the counter efficiency factor. The net counting rate, R_s, is given by the following:

$$R_s = \frac{n_g}{t_g} - \frac{n_b}{t_b}$$

where n_g and n_b are sample and background counts, respectively, and t_g and t_b are sample and background counting intervals, respectively. The standard deviation of the disintegration rate is expressed:

$$s = \left[\frac{n_g}{t_g^2} + \frac{n_b}{t_b^2} \right]^{\frac{1}{2}} YTE$$

where s is one standard deviation due to counting error.

The <u>recovery factor</u>, Y, is obtained by weighing the final precipitate and determining from this measurement the loss incurred through the chemical procedures. The calculation of the recovery factor is:

$$Y = \frac{x}{(w-t)\ f}$$

where x is the weight of lead added as carrier, w is the total weight of the final precipitate and filter paper, t is the weight of the filter paper, and f is the gravimetric factor which equals 0.641 mg lead per mg of lead chromate.

The precipitate thickness correction, T, is used to normalize self-absorption of the Bi^{212} and Po^{212} alpha activities in samples and standards to a common thickness. T is obtained by counting representative alpha activities within the energy range of 4.8 to 8.8 Mev through varying sample thicknesses. The correction is taken as the ratio of counting rates at the minimum thickness to other thicknesses over the range of probable sample recoveries. A composite plot of the correction obtained for Th^{230}, Pb^{212}, and Ra^{226} activities through varying thicknesses of their oxalate, chromate and sulfate derivatives, respectively, is illustrated in Procedure 5 (Figure 11).

The efficiency factor, E, is determined by alpha counting a standard of known equilibrated Ra^{226} activity under sample conditions. The correction is taken as the ratio of theoretical activity to observed counts. The calculation is expressed:

$$E = \frac{A}{R_s'T'}$$

where A is the theoretical activity of the standard, R_s' is the net counting rate of the standard, and T' is the thickness correction for the standard. The net counting rate of the standard, R_s', is given by the following calculation:

$$R_s' = \frac{n_g'}{t_g'} - \frac{n_b'}{t_b'}$$

where n_g' and n_b' are gross standard and background counts, respectively, and t_g' and t_b' are standard and background counting intervals, respectively.

The <u>Ra^{224} disintegration rate</u> is obtained from the Bi^{212}-Po^{212} disintegration rate through the following calculation:

$$(d/m\ Ra^{224}) = (d/m\ Bi^{212} + Po^{212})\ \frac{C_1 \times C_2}{D}$$

where C_1 is the theoretical ratio of Ra^{224} to Pb^{212} at equilibrium, C_2 is the theoretical ratio of Pb^{212} and Bi^{212} to Po^{212} at equilibrium and D is the decay factor used to correct for decay of Pb^{212}. The Bateman function for the ratio of Ra^{224} to Pb^{212} at equilibrium, C_1, reduces to the following:

$$C_1 = \frac{d/m\ Ra^{224}}{d/m\ Pb^{212}} = \frac{\lambda_{Pb} - \lambda_{Ra}}{\lambda_{Pb}} = 0.906$$

Similarly, the ratio of Pb^{212} and Bi^{212} to Po^{212}, C_2, reduces to 0.877. The decay constant, D, is expressed:

$$D = e^{-\lambda_{Pb}\Delta t}$$

where Δt is the interval between the separation of lead and radium and the final count.

Discussion

The method presented has been evaluated using experimental as well as actual samples. The radiometric purity of the chromate derivative has been ascertained through radioactive tracer studies and decontamination factors of 10^6 are routine for most radioactive contaminants. The ten-hour storage time permits the decay of Pb^{214}, Pb^{211}, and their alpha daughters with negligible buildup of Bi^{210} and Po^{210} from Pb^{210}. Recovery of lead from liter urine samples ranges from 70 to 80%.

Procedure 5

Determination of Radium-226 in Urine[84]

Principle

The radium-226 content of urine is determined by chemical isolation of radium and radiometric assay of the alpha activities of Ra^{226} and its daughter products. Radium is initially separated from untreated urine by coprecipitation with calcium phosphate. Calcium and uranium are removed by coprecipitation of radium with barium sulfate using ammonium sulfate. Organic material is removed by ignition. Silica is removed by volatilization from hydrofluoric acid.

Ra^{226} in the barium sulfate precipitate is stored to allow the buildup of Rn^{222}, Po^{218} and Po^{214}. The equilibrated alpha activities are then assayed with an alpha scintillation counter. Instrument response is converted to the disintegration rate by application of corrections for counter background, efficiency, self-absorption and recovery. Precision is expressed as one standard deviation due to counting error. The Ra^{226} disintegration rate is equivalent to one-fourth of the total disintegration rate measured.

Special Apparatus and Reagents

1. Zinc sulfide phosphor discs (See Procedure 4).
2. Barium carrier solution - 9.51 g $Ba(NO_3)_2$/1. in 1% HCl.

Sample Preparation and Determination

1. Transfer a measured volume of urine to a 250 ml. centrifuge bottle.
2. To the sample add 2 ml. of H_3PO_4. Adjust the pH to 9 with NH_4OH. Stir, centrifuge and discard the supernate.
3. Dissolve the precipitate with 10 ml. of HNO_3. Dilute to about 100 ml. with H_2O. Repeat step 2.
4. Dissolve the precipitate in a few ml. of acetic acid and dilute to 100 ml. with H_2O. Adjust the pH to 5 with NH_4OH. Add 1 ml. of barium carrier solution and 3-4 g of $(NH_4)_2SO_4$ with stirring. Digest for 12 hours. Cool and filter over Whatman #42 filter paper. Wash with 0.5% H_2SO_4. Discard filtrate and wash solutions.
5. Transfer precipitate and filter to a platinum dish. Dry and ignite at 900°C. Add 2 ml. of 1:1 H_2SO_4 and 5 ml. of HF. Evaporate on a sand bath until SO_3 fumes appear.
6. Transfer the solution to a 40 ml. centrifuge tube

with 30 ml. of H_2O and digest for 12 hours. Centrifuge and discard supernate.

7. Wash the precipitate with 10 ml. of H_2O. Centrifuge and discard wash solution.
8. Slurry the precipitate with water and filter over weighed glass fiber filter paper. Dry, weigh, mount under zinc sulfide phosphor disc. Store for 30 days and alpha count.

Calculations

The Ra^{226} disintegration rate is obtained from the counting rate of the equilibrated radium fraction through the following calculations:

$$d/m = R_s \, YTCE$$

where R_s is the net counting rate of the sample, Y is the recovery factor, T is the self-absorption correction, E is the counter efficiency factor and C is a theoretical conversion from total alpha activity to Ra^{226} alpha activity. The net counting rate, R_s, is given by the following:

$$R_s = \frac{n_g}{t_g} - \frac{n_b}{t_b}$$

where n_g and n_b are gross sample and background, respectively, and t_g and t_b are sample and background counting intervals, respectively. The standard deviation of this disintegration rate is expressed:

$$s = \left[\frac{n_g}{t_g^2} + \frac{n_b}{t_b^2}\right]^{\frac{1}{2}} \text{YTEC}$$

where s is one standard deviation due to counting.

The <u>recovery factor</u>, Y, is obtained by weighing the final sulfate precipitate and determining from this measurement a loss incurred through the chemical separation. The calculation of the recovery factor is:

$$Y = \frac{x}{(w-t)\ f}$$

where x is the weight of barium added as carrier, w is the total weight of the final precipitate and filter paper, t is the weight of the filter paper, and f is the gravimetric factor which equals 0.588 mg barium per mg of barium sulfate.

The <u>precipitate thickness correction</u>, T, is used to normalize self-absorption of the Ra^{226}, Rn^{222}, Po^{218} and Po^{214} alpha activities in samples and standards to a common thickness. T is obtained by counting representative alpha activities over the energy range of 4.8 to 8.8 Mev through varying sample thicknesses. The correction is taken as the ratio of counting rates at the minimum thickness to their thicknesses over the range of probable sample recoveries. Fig. 11 is a composite plot of the correction obtained for Th^{230}, Pb^{212} and Ra^{226} activities through varying thicknesses of their oxalate, chromate and sulfate derivatives, respectively.

The theoretical activity conversion factor, C, equals 0.25 after 30 days due to the buildup of three alpha daughters into secular equilibrium with Ra^{226}. However, the ratio of Ra^{226} to total alpha activity at any time after the separation of radium may be calculated from Bateman equations, provided contamination from the thorium series is negligible.

The efficiency factor, E, is determined by alpha counting a known quantity of Ra^{226} under sample conditions. The correction is taken as the ratio of theoretical activity to the observed counting rate. The calculation is expressed:

$$E = \frac{A}{R_s'T'C'}$$

where A is the theoretical activity of the standard, and R_s' is the net counting rate of the standard. T' is the self-absorption correction for the standard obtained from Fig. 11 and C' is the theoretical ratio of Ra^{226} alpha activity to total alpha activity in the standard (from Bateman equations). The net counting rate of the standard, R_s', is obtained from the following calculation:

$$R_s' = \frac{n_g'}{t_g'} - \frac{n_b'}{t_b'}$$

where n_g' and n_b' are gross standard and background counts, respectively, and t_g' and t_b' are standard and background counting intervals, respectively.

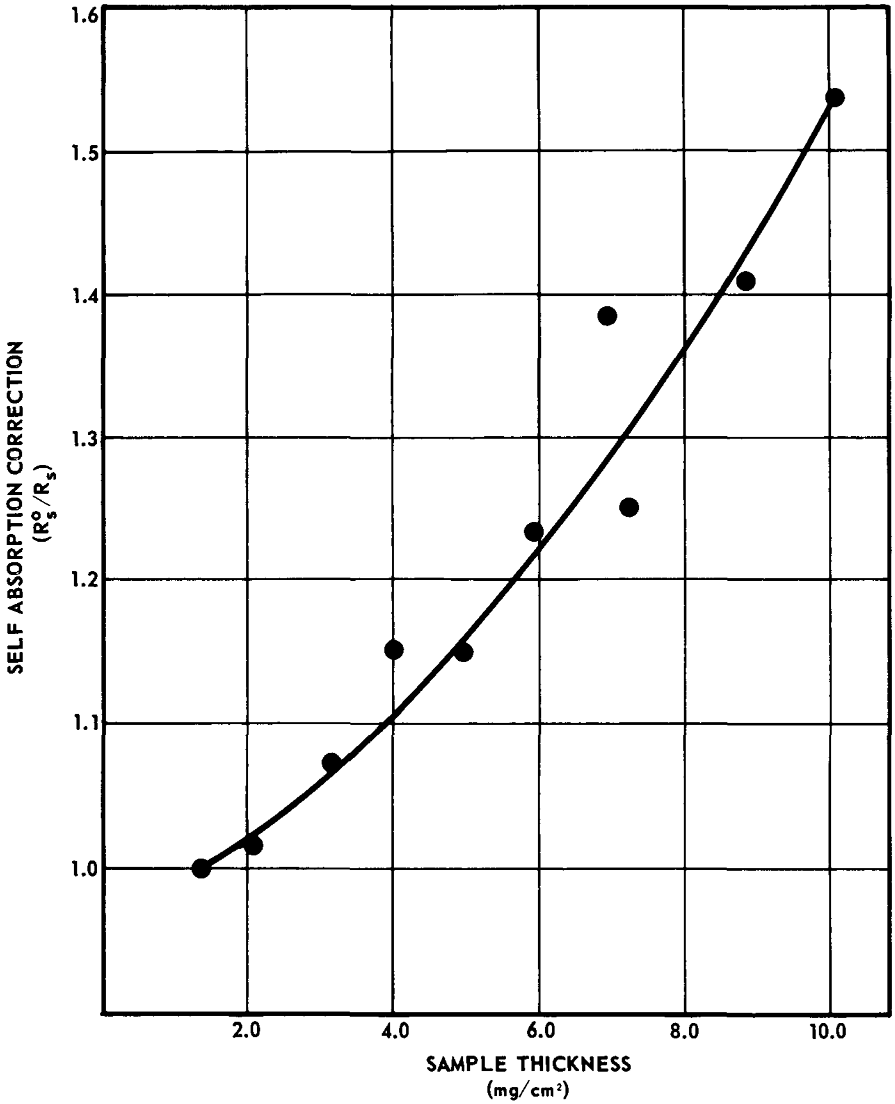


Fig. 11. Self absorption correction for alpha activities (4.8 - 8.8 MEV)

Discussion

The method presented has been evaluated using experimental as well as actual samples. The radiometric purity of the sulfate derivative is adequate for the determination of Ra^{226} in the presence of radioactive contaminants normally expected in urine.

However, the method is not applicable to samples enriched in Th^{230} or Ra^{224}. If contamination from the thorium series is present, it is necessary to store the barium sulfate precipitate for the recommended 30 days to allow the decay of Ra^{224} and its daughter products.

Reviewer's Note

Barium sulfate precipitates carry variable amounts (up to 100%) of actinium and thorium isotopes. When these nuclides are expected to be present, this procedure should not be used (See Procedure 6).

Procedure 6

Determination of Radium in Human Urine[69]

Principle

Radium is separated from actinium, thorium, and other actinides by coprecipitation with barium from 80% nitric acid.

Procedure

Obtain a 24-hour sample of urine, record its volume, and if the volume is less than 1800 milliliters dilute to 1800 milliliters with distilled water (Note 1). Transfer the urine to a 3000 milliliter beaker and begin stirring at a rate which will give good agitation without excessive foaming. Add one milliliter of 85 per cent phosphoric acid and 25 milliliters of concentrated ammonium hydroxide. Mix thoroughly and test the mixture with pH test paper. The pH should be nine or greater. If necessary, add five milliliter portions of concentrated ammonium hydroxide until the urine is at pH 9 to 10. Continue stirring for five to 10 minutes.

> Note 1. The sample should consist of all the urine passed in any 24-hour period rather than a specific volume. Both the first and last samples of each day usually contain abnormally high salt concentrations. By taking a true 24-hour sample, a sample is obtained which more nearly approximates the "average."

Transfer the suspension quantitatively to a 2000-milliliter graduated cylinder and allow it to settle for at least two hours. At the end of two hours, if the volume of precipitate is less than 350 milliliters, siphon off and discard the supernate. If at the end of two hours the precipitate is greater than 350 milliliters, allow it to settle until that volume is reached (Note 2).

> Note 2. The largest volume of precipitate which can conveniently be transferred to a pair of 250 milliliter centrifuge bottles is 350 milliliters. To avoid disturbing the precipitate it is usually necessary to leave approximately 100 milliliters of supernate above the precipitate. With the additional water used in making a quantitative transfer the total volume is very nearly 500 milliliters. If

the operator so desires, it is permissible to proceed at the end of two hours, even if the volume of precipitate is greater than 350 milliliters by dividing the slurry among three or four centrifuge bottles instead of two.

Occasionally the precipitate may settle to less than 100 milliliters. When this is the case, return the suspension to the 3000 milliliter beaker, add concentrated nitric acid until the solution is clear, then add 100 milligrams of calcium as calcium nitrate. Repeat the addition of ammonium hydroxide, stir, and return the suspension to the 2000-milliliter graduate. Allow the precipitate to settle for two hours.

Siphon off and discard the supernate. Transfer the precipitate quantitatively to two 250-milliliter centrifuge bottles. Centrifuge the precipitate at 1500 revolutions per minute (rpm) for 15 minutes. Siphon off and discard the supernates from both bottles. To the precipitate in one bottle, add five milliliters of concentrated nitric acid. Shake to dissolve the precipitate, then transfer the solution quantitatively to the other centrifuge bottle. Dilute the mixture with distilled water until the volume is approximately 100 milliliters. Stir vigorously until all lumps are either broken up or dissolved. Add, while stirring vigorously, 10 milliliters of concentrated ammonium hydroxide.

Stir five minutes, centrifuge 15 minutes at 1500 rpm, siphon off and discard the supernate.

To the precipitate add 25 milliliters of concentrated nitric acid and shake or stir the precipitate until it is dissolved. Transfer the solution quantitatively to a 100-milliliter beaker previously marked at the three-milliliter level.

Add to the solution ten milligrams of barium as barium nitrate. Cover the beaker with a ridged watch glass, and evaporate the solution on a hot plate. Carry out the evaporation in a fume hood with a good draft, and exercise caution to avoid bumping or spattering.

When the solution has evaporated to a volume of three milliliters add 10 milliliters of concentrated nitric acid, and repeat the evaporation. When the volume again reaches three milliliters, remove the beaker from the hot plate, and allow it to cool to room temperature. If the solution has accidentally evaporated to dryness, add five milliliters of concentrated nitric acid, and repeat the evaporation.

When the solution has cooled to about room temperature, add three milliliters of red fuming nitric acid. Stir gently until the evolution of gases has stopped. Place the beaker in an ice bath for 15 minutes. Stir the precipitate occasionally.

Transfer the slurry to a previously cooled 50-milliliter graduated centrifuge cone. Wash the beaker twice with one-milliliter portions of concentrated nitric acid. Add the washes to the slurry in the centrifuge tube (Note 3). Any crystals clinging to the sides of the centrifuge tube should be rinsed down with a few drops of concentrated nitric acid. Place the centrifuge tube and its trunnion cup in the ice bath for five minutes. Record the time at the end of the cooling period.

Note 3. It is not necessary to transfer the precipitate quantitatively to the centrifuge tube; the untransferred precipitate is recovered later in the procedure.

Centrifuge the precipitate for five minutes at 1800 rpm (Note 4). Decant the supernate into a 250-milliliter beaker. Rinse the sides of the 100-milliliter beaker four times with one-milliliter portions of concentrated nitric acid. Transfer the washes to the centrifuge tube. Stir the slurry in the centrifuge tube for one minute or until the precipitate is completely broken up and the slurry is homogeneous. Touch off, but do not wash, the stirring rod. Rinse the precipitate down from the sides of the centrifuge tube with a few drops of concentrated nitric acid. Centrifuge the precipitate one or two minutes at 1800 rpm. Decant the supernate into the 250-milliliter beaker (Note 5).

Note 4. The volume of the slurry will be between 8 and 10 milliliters. In balancing the tubes if more than one sample is being run, it is preferable to balance each sample tube against a blank tube containing water, unless they can be balanced against each other by the addition of a few drops of concentrated nitric acid.

Note 5. The contents of the 250-milliliter beaker are reserved for actinide analysis. If only radium isotopes are being determined, this solution may be discarded.

Wash the 100-milliliter beaker several times with small portions of distilled water. Add the washes to the precipitate in the centrifuge tube. Repeat the washing until the volume in the centrifuge tube is 20 milliliters. With the stirring rod first used for stirring the barium nitrate precipitate, stir until the precipitate in the centrifuge tube is completely dissolved.

To the solution add one drop of 85 per cent phosphoric acid (or one milliliter of approximately one molar phosphoric acid), one drop of 0.1 per cent methyl orange solution, and one milligram of cerium as cerous nitrate. While stirring vigorously, add concentrated ammonium hydroxide dropwise until the color change indicates pH 4 to 5. If necessary, adjust the pH by addition of one normal nitric acid or one normal ammonium hydroxide.

Stir the precipitate five minutes. Centrifuge five minutes at 1800 rpm, and decant the supernate to a second centrifuge tube. Add to the precipitate 10 milliliters of a one per cent solution of ammonium dihydrogen phosphate. Stir vigorously for five minutes or until the precipitate is completely broken up and the slurry is homogeneous. Rinse the stirring rod and the sides of the centrifuge tube with a little distilled water. Centrifuge five minutes at 1800 rpm and add the wash to the supernate. Discard the precipitate.

To the combined wash and supernate, add 0.1 milliliter of concentrated sulfuric acid (or one milliliter of approximately 10 per cent sulfuric acid) and stir 15 minutes. Centrifuge five minutes at 1800 rpm, and discard the supernate. Add to the precipitate 10 milliliters of distilled water, and stir the slurry for five minutes. Centrifuge and discard the wash. Transfer the precipitate to a counting disk as a slurry in one normal nitric acid (Note 6).

Note 6. Samples are mounted on stainless steel disks 1-7/8 inch in diameter and 0.018 inch thick. Before use the disks are washed in a solution of a detergent, rinsed with distilled water, and dried. Since aqueous solutions do not spread well on bright stainless steel, the disk is held in the flame of a Meker Burner until the surface is slightly oxidized (color of brass). The disk is allowed to cool, and a ring of Zapon lacquer, two to five millimeters wide, is applied with a brush to the outer edge. The Zapon is dried under an infrared lamp, and the disk is allowed to cool. The slurry of barium sulfate may then be transferred with the aid of a transfer pipet to the area within the lacquer ring. As many as three one-milliliter washes with one normal nitric acid may be added without danger of overflowing.

Evaporate the liquid under an infrared lamp. When the sample is dry, ignite it at red heat in the flame of a Meker burner for about 15 seconds. Note the time of ignition, and allow the sample to cool.

Count the sample in a low-background alpha counter beginning not less than six hours after ignition.

Discussion

Experiment has shown that radon loss from ignited barium sulfate is negligible. The growth of radium isotopes may, therefore, be considered as taking place with 100 per cent radon retention. If the time between the cerium phosphate precipitation and the barium sulfate ignition is made as short as possible (less than one hour), no significant error will result from considering the ignition time as zero time for all the radium isotopes. The time of precipitation of the barium nitrate represents the time of separation of radium-223 and radium-224 from actinium-227 and thorium-228 respectively. If this time is very different from the time of barium sulfate ignition, an extrapolation should be made to determine the amount of each radium isotope present before separation.

Correction should be made for self-absorption of the sample. Ten milligrams of barium as sulfate spread over the area specified (Note 6) will absorb about 15 per cent of the alpha counts from the three radium isotopes and their decay products.

Analysis of the barium sulfate precipitate for radium isotopes is carried out by the method of differential decay.[79]

Procedure 7

Determination of Radium-226 in Human Urine[103]

Principle

Radium is separated from other radioelements by coprecipitation with barium chloride from cold HCl-ether mixture.

Reagents

1. Nitric acid, concentrated and dilute (0.1M).
2. Lead carrier, 200 mg per ml (as Pb); 32 grams of $Pb(NO_3)_2$ are diluted to 100 ml.
3. Barium carrier, 10 mg (as Ba); 1.9 grams of $Ba(NO_3)_2$ are diluted to 100 ml.
4. Sulfuric acid, concentrated, and dilute (0.5M).
5. HCl-ether reagent, which consists of six parts, by volume, of concentrated HCl and one part of ethyl ether.

Procedure

Sample To a 24-hour urine sample add 100 ml of concentrated HNO_3 and evaporate to dryness on a hot plate. Cool, add about 20 ml additional HNO_3 and evaporate again. Repeat until a white ash is obtained (Notes 1, 2). Add 150 ml of 0.1 M HNO_3, warm for five minutes, transfer solution to a 250-ml centrifuge bottle. Centrifuge and transfer supernatant to a second 250-ml centrifuge bottle. Rinse beaker with 50 ml of 0.1M HNO_3, use washings to wash precipitate in first centrifuge bottle. Centrifuge and combine both supernatants. To the combined supernatants add dropwise, while stirring mechanically with a platinum wire, 3 ml of concentrated H_2SO_4 followed by dropwise addition of 0.50 ml of lead carrier. Immerse the bottle in a bath of ice water and continue stirring for 15 minutes. Centrifuge. Discard solution.

Precipitate $PbSO_4$ plus Ra^{226}. Dissolve by gently warming with 15 ml of HCl-ether reagent. Transfer solution quantitatively to a 50-ml centrifuge tube using a total of 10 ml of HCl-ether reagent for washing. Cool tube in ice bath. Add 0.40 ml of barium carrier while stirring. Continue to stir for five minutes. Centrifuge in ice-packed cups for five minutes. Discard solution.

Precipitate $BaCl_2$ plus Ra^{226}. Add 1 ml of 0.1-1M HNO_3, expedite solution of precipitate by disintegrating precipitate with a platinum rod, transfer slurry with a capillary pipet to a platinum plate ringed with Zapon lacquer (Note 3), evaporate under infra-red lamp for 2-3 minutes, add 4 drops of 0.5M H_2SO_4

and evaporate to dryness (Note 4). Flame the plate carefully over a small flame to burn off lacquer border; then flame to red heat over a Meker burner. Count the deposit in an alpha counter.

Notes

1. The time required for ashing is 4-6 hours. Subsequent steps take less than an hour. The ashing procedure insures complete removal of radon, and allows time for the decay of the short-lived alpha-daughter activities.

2. Feces may be wet ashed by modifying the procedures as follows: Dry the feces at 80°-100°C overnight, place in muffle furnace and heat at 450°-500°C for an additional 24 hours. Then ash residue with HNO_3 as described for urine.

3. The platinum plates are about 4 cm in diameter. The approximate diameter of the deposited sample is 3.5 cm. The Zapon lacquer is applied in a margin 2-4 mm wide around the edge of the disc. When dry, it prevents the solution from running off. The platinum discs are re-used after removing the radium deposit. This is done by heating the discs overnight or longer in fuming sulfuric acid which forms a soluble sulfate complex by reaction with $RaSO_4$. Glass plates about 4 cm in diameter and 2-3 mm thick have been used routinely and have the advantage that they may be discarded after each analysis. They may be purchased from the Scientific Glass Apparatus Co. The Zapon lacquer is made by the Zapon Division, Atlas

Powder Company, North Chicago, Illinois. The lacquer is thinned with a small amount of acetone before use.

4. The residue as prepared for direct counting is uniform and adhering. Previous attempts to develop a direct count method with $BaCl_2$ but without the addition of H_2SO_4 for use with tissues were unsatisfactory, largely because of splattering and of the formation of irregular deposits.

Procedure 8

Determination of Radium in Urine[86]

Principle

Radium is cocrystallized from urine with potassium rhodizonate and purified by cation exchange.

Procedure

1. To an aliquot of a 24-hour urine collection (100 to 200 ml) adjusted to pH 5 to 7, is added solid potassium rhodizonate to make a concentration of 1%. If necessary, warm the sample to solubilize the reagent. Cool to room temperature.
2. Add slowly and with stirring 15 ml of ammonium chloride (0.2 g/ml) reagent per 100 ml of sample.
3. Let stand five minutes and separate the crystals by filtration.
4. Dissolve crystallized rhodizonate in 20 ml of 4<u>N</u> nitric acid and dilute to 200 ml.
5. Pass this solution through the column. (The resin bed consists of 50 to 100 mesh Dowex 50-X8 in the H^+ form in a

glass column 10 cm long and 0.6 cm inside diameter. The flow rate is 2-4 ml/min.) Wash with 50 ml of water followed by 100 ml of a Versene citric acid solution, pH 5.1. (To 100 ml of 7.5% Versene, add 10.93 grams of citric acid monohydrate, dilute to one liter with distilled water and adjust the pH to 5.1 with 6N sodium hydroxide.)

6. Wash the column with 100 ml of 0.2N nitric acid and elute the radium with 100 ml of 4N nitric acid.
7. Evaporate the eluate to dryness and ash the residue over a flame.
8. Wash the walls of the ashing vessel with about 5 ml of concentrated nitric acid, add several ml of concentrated perchloric acid and reduce the volume to about one ml.
9. Transfer the solution to a platinum disc (2.1 cm diameter) and dry on a hot plate. Flame the dried disc for 30 seconds.
10. Count a minimum of four hours after flaming and correct the counting data for daughter growth.

Results

Eleven samples of urine, 200 ml in volume, to which were added from 6 x 10^{-12} to 1.5 x 10^{-9} curies of radium-226 were submitted to analysis by this procedure. The average recovery was 94.9% with a standard deviation of 3.3%. By tracing with radium-223, the loss was determined to occur primarily in the evaporation steps.

The final residue weight ranges from 0.2 to 0.5 mg. With residue weights of this magnitude, errors due to self-absorption are negligible. Further, if desired, this condition permits positive identification by pulse-height analysis since the mass is insufficient for attentuation of the alpha particles. In this connection, examination of the degree to which other alpha emitters follow the procedure indicated that uranium and plutonium were completely discriminated against while about 20% of both thorium and protactinium was recovered

Procedure 9

Isolation of Radium in Biological Materials[80]

Principle

To insure complete dissolution of radium, the sample is first wet-ashed with nitric acid, then ignited in a muffle furnace. Procedure 10 is followed for isolation of the radium.

Reagents for Pretreatment of Samples

Ammonium hydroxide, 6 normal

Ammonium hydroxide, 10 per cent

Ammonium hydroxide, concentrated

Hydrochloric acid, 10 per cent

Citric acid, 3 normal

Nitric acid, concentrated

Lead nitrate; 100 mg Pb^{++}/ml

Barium nitrate, 25 mg Ba^{++}/ml

Detergent solution, 30 gm/1

1. Pretreatment of Water Samples

Measure 1000 ml of the water sample into a 2-liter beaker. Add 50 ml of concentrated HNO_3 and 25 mg of Ba carrier. Place the beaker on the hot plate. Bring to a simmer, just under boiling, for 1/2-1 hr. Remove beaker from hot plate and let cool. To beaker add conc NH_4OH, with stirring, to a pH of 7.0-7.5. To the beaker add the following reagents in the following order:

a. 5 ml of 3N citric acid;
b. 2.5 ml of conc NH_4OH;
c. 200 mg Pb carrier.

2. Pretreatment of Milk Samples

Weigh out 100 gm of milk and pour into a large quartz dish. To the quartz dish add 25 mg Ba carrier. Place the quartz dish on a hot plate, evaporate to dryness, and ignite.

Place the quartz dish in a preheated muffle furnace (at 650°C). Keep the door slightly open and muffle for 10 min. Close the muffle door and muffle for approximately 2 hr at a temperature of 650°C. Remove from the muffle furnace and cool.

To the quartz dish add 100 ml conc HNO_3 and evaporate to dryness on a hot plate. Place quartz dish in the muffle furnace at 650°C. Keep the door slightly open until the nitric acid fumes are gone. Close the muffle furnace door and muffle for approximately 1-1/2 hr at 650°C. Repeat HNO_3 addition and muffling until a white ash is obtained. Remove the quartz dish from the muffle furnace and cool.

To the quartz dish add 100 ml of 10% HCl. Heat approximately 15 min (ash should be in solution). Transfer into a 2-liter beaker, rinsing the quartz dish with distilled water. Repeat HCl addition, heat, transfer and wash. Bring the final volume in the beaker to 1 liter by addition of distilled water.

To the beaker add 6<u>N</u> NH_4OH, with stirring, to a pH of 7.0-7.5. Add the following reagents in the following order:

a. 5 ml of 3<u>N</u> citric acid;

b. 2.5 ml of conc NH_4OH;

c. 100 mg Pb carrier.

3. <u>Pretreatment of Urine Samples</u>

Take complete daily sample of urine and place into as many 500-ml centrifuge bottles as needed. Add 6<u>N</u> NH_4OH to pH of 10, centrifuge 45 min, discard supernatant. Add 20 ml of 10% NH_4OH to each bottle. Centrifuge for 30 min. Discard supernatant.

Add 20 ml of 10% HCl to the precipitate and heat to dissolve the precipitate. Transfer solution to a 2-liter beaker. Rinse bottle with an additional 20 ml of 10% HCl and, finally, with distilled water. Add these rinsings to beaker. Adjust final volume to 1 liter with distilled water.

Add 6N NH_4OH, with stirring, to pH 7.0-7.5. Add the following reagents in the following order:

a. 5 ml of 3N citric acid;

b. 2.5 ml of conc NH_4OH;

c. 100 mg Pb carrier;

d. 25 mg Ba carrier.

4. Pretreatment of Fecal Samples

Remove samples stored in freezer or cold room. Take the complete daily sample and place in a quartz dish. Heat on hot plate until charred or taken to dryness; then ignite.

Place the quartz dish in the muffle furnace with the door slightly open at a temperature of 600-650°C until complete ignition is achieved (approximately 10 min). Close the doors, then muffle for approximately 16 to 18 hr at 650°C. Remove from muffle furnace and cool.

Add 100 ml conc HNO_3 to the quartz dish by means of a pipette. (A pipette is used so that the sides of dishes can be washed down with HNO_3.) Take to dryness on a hot plate.

Place the quartz dish in a preheated (650°C) muffle furnace for approximately 10 min with the door slightly open. Close the door and muffle for 1-1/2 - 2 hr at 650°C. Repeat HNO_3 addition and muffling until a white ash is achieved. Remove from the muffle furnace and cool.

Add 50 ml of 10% HCl to the dish and heat on a hot plate until ash is in solution. Transfer the solution to a 2-liter beaker, rinsing with distilled water. Repeat HCl addition and transfer.

Adjust the final volume to 1 liter with distilled water. Add 6$\underline{N}$ NH_4OH, with stirring, to a pH of 7.0-7.5. Add the following reagents in the following order:

a. 5 ml of 3$\underline{N}$ citric acid;

b. 2.5 ml of conc NH_4OH;

c. 100 mg Pb carrier;

d. 25 mg Ba carrier.

5. Pretreatment of Blood Samples

Remove blood sample from cold room storage and leave overnight to come to room temperature. Weigh the test tube containing the blood sample. Rinse the blood from the tube, with distilled water, into a platinum-clad crucible. Make sure all the blood is removed.

Dry the tube, weigh it, and subtract this from the weight of the tube and the blood. This will give the weight of the blood sample.

To the platinum-clad crucible add 25 mg Ba carrier. Take to dryness on the hot plate. Exercise care, as blood will tend to spatter when almost dry. Use low heat.

Place the crucible on the edge of preheated (300-350°C) muffle furnace with the door wide open for approximately 15 min. Close the door and muffle for approximately 1-1/2 - 2 hr. Remove the crucible from the muffle furnace and cool.

Add 20 ml of conc HNO_3 to the crucible. Place on the hot plate and take to dryness, using low heat. Place in a preheated (600-650°C) muffle furnace for approximately 10 min with the door slightly open. Close the door and muffle for 1-1-1/2 hr at 650°C. Remove from the muffle furnace and cool. Repeat HNO_3 addition and muffling. Add 50 ml of 10% HCl to the crucible. Heat on hot plate and transfer to a 2-liter beaker. The ash should go into solution at this point. Repeat HCl addition and transfer.

Add 6$\underline{N}$ NH_4OH, with stirring, to a pH of 7.0-7.5. Add the following reagents in the following order:

a. 5 ml of 3N citric acid;

b. 2.5 ml of conc NH_4OH;

c. 100 mg Pb carrier.

6. Pretreatment of Human Hair Samples

Place the sample in a Petri dish, and place the dish and sample in a drying oven at a temperature of 100-105°C; dry overnight. Weigh the sample after drying.

Place the sample in a large funnel. Place the hair sample in a rapid-flow filter paper set in a large funnel. Wash with two 100-ml portions of detergent. Rinse with two 100-ml portions of distilled water. Place the filter paper containing the washed hair in a small quartz dish. Heat on a hot plate until the sample is dry.

Add 50 ml conc HNO_3 to the quartz dish and take to dryness on the hot plate. Place the dish in a preheated (650°C) muffle furnace with the door slightly open for 10 min. Close the door and muffle for 1-1-1/2 hr at 650°C. Remove from the muffle furnace and cool. Repeat HNO_3 addition and muffling.

Add 50 ml of 10% HCl and heat on the hot plate until ash is in solution. Transfer the contents to a 2-liter beaker, washing with distilled water. Repeat HCl addition and transfer. Adjust final volume to 1 liter with distilled water.

Add 6N NH_4OH, with stirring, to a pH of 7.0-7.5. Add the following reagents in the following order:

a. 5 ml of 3N citric acid;

b. 2.5 ml of conc NH_4OH;

c. 100 mg Pb carrier;

d. 25 mg Ba carrier.

7. Pretreatment of Brazil Nut Samples

Weigh the Brazil nuts and place the weighed portion in a Waring Blendor and grind. Transfer the ground sample into a quartz dish, using distilled water.

Place the quartz dish on a hot plate and evaporate to dryness; ignite. Place the quartz dish in a muffle furnace for approximately 10 min with the door slightly open. Then close the door and muffle at 650°C for 2 - 2-1/2 hr. Remove the quartz dish from the muffle furnace and cool.

Add 50 ml conc HNO_3 to the quartz dish, using a pipette. Take the sample to dryness on the hot plate. Place the quartz dish in a preheated (650°C) muffle furnace for approximately 10 min with the door slightly open. Close the door and muffle for 1-1/2 - 2 hr at 650°C. A white ash should result. Repeat HNO_3 addition and muffling. Remove the quartz dish from the muffle furnace and cool.

Add 50 ml of 10% HCl to the quartz dish. Heat on a hot plate until ash is in solution. Transfer the contents to a 2-liter beaker, using distilled water as a wash. Repeat HCl addition and transfer. Adjust the final volume in the beaker to 1 liter with distilled water.

Add 6N NH_4OH, with stirring, to pH of 7.0-7.5. Add the following reagents in the following order:

a. 5 ml of 3N citric acid;

b. 2.5 ml of conc NH_4OH;

c. 100 mg Pb carrier;

d. 25 mg Ba carrier.

8. Pretreatment of Food Samples (coffee beans, cocoa beans, and banana flakes)

Weigh the sample and place in a quartz dish. Place the quartz dish on a hot plate and heat until the sample is charred. (Ignition on a hot plate is not feasible with these samples.) Place the quartz dish in a preheated muffle furnace. Exercise care with banana flakes and ground coffee, as these samples tend to splatter. Heat for approximately 15 min with the door open. Close the door and muffle for 3-4 hr at 650°C. It may sometimes be necessary to muffle overnight, depending on the original weight of the sample. Remove the quartz dish from the muffle and cool.

Add 50 ml concentrated HNO_3 to the quartz dish and take to dryness on the hot plate. Place the quartz dish in the muffle furance with the door slightly open for approximately 10 min. Close the door and muffle at 650°C for 1 - 1-1/2 hr. Repeat HNO_3 addition and muffling. Remove the quartz dish from the muffle furnace and cool.

Add 50 ml of 10% HCl to the quartz dish and heat on a hot plate, until the ash is in solution. Transfer the contents of the quartz dish into a 2-liter beaker, using distilled water as a wash. Repeat HCl addition and transfer. Adjust the final volume in the beaker to 1 liter, using distilled water.

Add 6$\underline{N}$ NH_4OH, with stirring, to pH of 7.0-7.5. Add the following reagents in the following order:

a. 5 ml of 3$\underline{N}$ citric acid;

b. 2.5 ml of conc NH_4OH;

c. 100 mg Pb carrier;

d. 25 mg Ba carrier.

Reagents for Radium Chemistry

Sulfuric acid, 18 normal

0.1% Methyl orange

Nitric acid, conc

Ethylenediaminetetraacetic acid (EDTA, $\underline{M}$/4), disodium salt

Ammonium hydroxide, 6 normal

Acetic acid, glacial

Procedure

Heat the solutions obtained from the pretreatment of samples to boiling. To the hot solutions, add 5 to 10 drops of methyl orange indicator. Then add 18N H_2SO_4 slowly and with stirring to a pH of 1.5. A pink color should obtain. Rinse and remove stirring rods.

Digest for one hour on a hot plate. Remove from hot plate and allow to cool overnight.

Filter through prepared Gooch crucibles, using suction (Note 1). Wash precipitate in crucible with three 10-ml portions of conc HNO_3. Wash precipitate in crucible with one 20-ml portion of distilled water.

Transfer the crucible and contents to a 400-ml beaker and add:

a. 20 ml distilled water;

b. 20 ml M/4 EDTA;

c. 10 ml 6N NH_4OH (Note 2).

Heat solution to boiling and keep just under boiling until all the precipitate dissolves. Keep pH greater than 10 by adding 6N NH_4OH as required (Note 3). Rinse crucible with distilled water and remove from beaker (Note 4). Check beaker to be sure all precipitate is in solution.

While hot, filter through large-size (18.5-cm) Whatman No. 40 paper. Catch the filtrate in another 400-ml beaker.

To the original 400-ml beaker add the following:

a. Gooch crucible;

b. 10 ml distilled water;

c. 10 ml M/4 EDTA;

d. 5 ml 6N NH_4OH.

Heat to boiling and repeat crucible rinse. Maintain a pH of 10.

Filter while hot onto filter paper containing asbestos and collect filtrate in beaker used for previous filtrate (See Note 5).

Heat combined filtrates to just under boiling and simmer for 10-15 min (Note 6). To hot solution add glacial acetic acid dropwise and with stirring to pH 4.5-4.0. Rinse and remove stirring rods. Note and record date and time (Note 7). If precipitate does not form, a few drops of 18N H_2SO_4 may be added. Care must be taken to keep pH above 3.5. Allow the precipitate to settle overnight.

Filter through Whatman No. 42 ashless filter paper (15 cm). Rinse and scrub beaker with distilled water and rubber policeman (Note 8).

Transfer filter paper and precipitate to platinum crucible and char off paper under an infrared lamp (Note 9). Transfer platinum crucible to muffle and heat at 650-700°C for 1 - 1-1/2 hr. Cool in desiccator and weigh.

Notes

1. It is essential that Gooch crucibles be prepared in the following manner:
    a. Add enough asbestos suspension to crucibles so that an even mat is obtained upon applying suction.
    b. Dry crucibles in oven at 100°C for approximately 30 min to 1 hr, and muffle at 650°C for half an hour. This step insures a better mat and allows a better distinction to be made between the asbestos and the precipitate.
    c. All the precipitate must be removed from beakers by means of distilled water and rubber policeman.

2. Use large amount of EDTA (50 ml more than usual) if large amount of precipitate is anticipated.

3. a. Asbestos and precipitate will tend to loosen after solution becomes hot. No attempt should be made to "dig" precipitate and asbestos from crucible.
    b. Precipitate will tend to settle to the bottom while asbestos tends to suspend in solution.
    c. Stirring vigorously will tend to speed solution of precipitate.
    d. Approximately one-half hour will suffice for complete solution.

4. Forceps may be used to remove crucible from solutions. At this point, a wash with sufficient force will remove any remaining asbestos and precipitate from the crucible. Be sure that washings go into beaker and rinse inside and outside of crucible wall before removing from the beaker.

5. This step will tend to dissolve any remaining precipitate that might remain with the asbestos.

6. Simmering at this point will drive off radon and allow radon daughters to decay to radium D.

7. This is the zero time. From this time ingrowth of radium daughters will occur.

8. a. The residual ash weight of the filter paper should be recorded so that it can be subtracted from the final weight.
   b. When filtering, the solution should not be allowed to go over half the volume of the funnel due to the creeping nature of $BaSO_4$.
   c. Check filtrate for any signs of precipitate.

9. a. Charring while the paper is wet is quicker.
   b. Be sure paper does not burst into flame.

(Reviewer's note: The $BaSO_4$ may now be transferred to a planchet for counting or treated as described in Section V, page 39)

Procedure 10

Determination of Dissolved Radium[104]

Principle

Lead and barium carriers are added to a solution containing alkaline citrate, which prevents precipitation until complete isotopic exchange is effected. Sulfates are precipitated, redissolved with EDTA, and reprecipitated with acetic acid.

Reagents

$Ba(NO_3)_2$, 0.10N

$Pb(NO_3)_2$, 1N

Citric Acid, $H_3C_6H_5O_7$, 1M (should contain 0.1% phenol to prevent biological growth).

Procedure

Add about five ml of citric acid to the sample and make it alkaline with ammonium hydroxide. Add two ml of lead carrier and one ml of barium carrier. Heat to boiling and add sufficient sulfuric acid (1 to 1 by volume) to precipitate substantially all the lead. (This may be done by adjusting to pH 1 with a meter, by adding about 0.25 ml in excess after neutralizing to methyl orange or methyl red, or simply visually by the amount of precipitate.) Collect the precipitate; wash it twice with concentrated nitric acid. Dissolve the precipitate in alkaline EDTA (disodium salt, 0.25M) and reprecipitate the barium sulfate by dropwise addition of glacial acetic acid in excess. When necessary, repurify the barium sulfate by a second solution in alkaline EDTA and reprecipitation with acetic acid. In this case, add a little ammonium sulfate to the EDTA solution to ensure complete precipitation. Wash the barium sulfate precipitate and transfer to a planchet for counting.

(See also Procedure 43, page 230)

Procedure 11

Determination of Radium in Uranium Process Samples[58]

Principle

Radium is coprecipitated with lead sulfate, converted to carbonate, and reprecipitated with fuming nitric acid. The lead is adsorbed on an anion exchanger, yielding carrier-free radium.

Procedure

This procedure is suitable for carbonate or sulfuric acid solutions and phosphoric acid solutions resulting from the dissolution of solid samples.

Adjust 500 ml of the clarified sample to pH 1 with concentrated nitric acid and heat to 70°C. While stirring with a Teflon-coated magnetic stirring bar, add 5 ml of 0 49$\underline{M}$ lead nitrate solution (100 mg of Pb^{+2} per ml). Add, very slowly, 60 ml of 9$\underline{M}$ sulfuric acid (1 to 1). Stir continuously for 1 hour, allow the precipitate to settle, and discard the supernatant solution by careful decantation.

$$Pb^{+2} + SO_4^{-2} + \text{sample at pH 1} \longrightarrow Pb(Ra)SO_4$$

Transfer the precipitate to a 50-ml centrifuge tube using 1M sulfuric acid. Centrifuge and discard the supernatant liquid. Add five ml of 6M ammonium acetate to dissolve the lead sulfate. Add 25 ml of 25% sodium carbonate solution and stir occasionally for 15 minutes.

$$Pb(Ra)SO_4 + CO_3^{-2} \longrightarrow Pb(Ra)CO_3 + SO_4^{-2}$$

Centrifuge, discard the supernate, and add 3M nitric acid until effervescence ceases. Add water and heat to dissolve the salts. The total volume after addition of acid and water should be approximately 5 to 7 ml. If at this point of the procedure all the salts are not in solution after heating, add 25 ml. of 25% sodium carbonate solution; stir for 15 minutes; centrifuge and discard the supernate and redissolve in nitric acid. When the salts are dissolved, place the centrifuge tube in an ice bath; add 30 ml. of red fuming nitric acid and stir. Cool, centrifuge and discard the supernatant liquid.

$$Pb(Ra)CO_3 + 2HNO_3 \longrightarrow Pb(Ra)^{+2} + 2NO_3^- + CO_2 + H_2O$$

$$Pb(Ra)^{+2} + 2NO_3^- \xrightarrow[HNO_3]{\text{red fuming}} Pb(Ra)(NO_3)_2$$

Place the centrifuge tube in a water bath and spread the solid material to prevent splattering. Heat to drive off excess acid, add 30 ml. of water, and heat, if necessary to dissolve the salts. Add 5 ml. of concentrated hydrochloric acid dropwise (stirring constantly) to precipitate lead chloride, and cool in an ice bath. Centrifuge and pass the supernatant solution over a column of 15 ml. of Dowex 1-X8, 100- to 200-mesh anion exchange resin, suspended in 1.8M hydrochloric acid (1 to 6). Use a flow rate of 1 ml. per minute and collect the effluent in a 150-ml. beaker. The column is most conveniently constructed from a standard 25-ml. buret.

$$PbCl_x^{2-x} + Ra^{+2} + \text{resin} \xrightarrow{1.8\underline{M}\ HCl} \text{resin} - (PbCl_x^{2-x}) + Ra^{+2}$$

Add 35 ml. of water to the lead chloride precipitate and heat in a water bath with stirring until the solid dissolves. Add 6 ml. of concentrated hydrochloric acid dropwise (stirring constantly). Cool in an ice bath and centrifuge. Pass the supernatant solution over the same resin bed, and wash the resin bed with an additional 15 ml. of 1.8M hydrochloric acid. Collect and combine all resin bed effluents and discard the lead chloride precipitate.

Evaporate the effluent to dryness, but do not bake. Add 10 ml. of nitric acid and evaporate to dryness to destroy organic matter from the resin.

Wash the beaker with small volumes of 1M nitric acid and transfer to a 10-ml. volumetric flask. Evaporate a 0.2-ml. aliquot on a stainless steel planchet and count for alpha activity.

Count the samples immediately. If this is not possible, boil the sample for 2 to 3 hours before diluting to final volume.

Procedure 11a

Radiochemical Determination of Radium in Uranium Milling Process Samples[45]

Principle

Two modifications are made to Procedure 11: ammonium carbonate is substituted for sodium carbonate and solvent extraction replaces ion exchange.

Apparatus and Reagents The counting equipment is a Nuclear Measurement Corp. PCC-10A proportional counter used in conjunction with a Technical Measurement Corp. SG-24A scaler.

Lead carrier, 0.49M lead nitrate solution.

100% active Aliquat 336 (General Mills Co., Kankakee, Ill.), 30% by volume dissolved in benzene. This solvent is washed three times in equal volumes of 4M NaOH and then three times in equal volumes of 1.5M HCl.

Solvent Extraction Modification After adding 4 ml. of concentrated hydrochloric acid dropwise (stirring constantly) to precipitate lead chloride and cooling the solution in an ice bath, centrifuge, and pour the supernate into a 250-ml. separatory funnel containing 100 ml. of the washed Aliquat 336-benzene solvent. Shake for 2 minutes, allow the phases to disengage, and draw off the aqueous phase into a 250-ml. beaker.

Add 15 ml. of 1.5M hydrochloric acid to the centrifuge tube containing the lead chloride precipitate. Stir well and cool in an ice bath. Centrifuge and pour supernate into the separatory funnel containing the Aliquat 336 solvent. Shake for 2 minutes, allow phases to disengage, and draw off the aqueous phase into the 250-ml. beaker containing the initial hydrochloric acid raffinate. Discard the lead chloride precipitate and the solvent.

Evaporate the combined hydrochloric acid raffinates to dryness. Charring, resulting from dissolved organic material, may result at this point. Place the beaker in a muffle furnace, adjusted to 500° to 600°C., and bake for 10 minutes to destroy organic material. Remove beaker from the furnace, allow to cool, and add 10 ml. of concentrated nitric acid. Evaporate the nitric acid to a volume of about 1 ml. on a low hot plate. Transfer the solution to a 10-ml. volumetric flask with the aid of small volumes of 1M nitric acid. Before making the last transfer, carefully clean the bottom of the beaker with a rubber policeman. Evaporate an aliquot of the sample on a 2-inch cup-type stainless steel planchet and count immediately for alpha activity.

For this procedure, the radium yield is 95% when starting with either liquid or solid samples, if a 1-ml. aliquot is mounted for counting. If the entire sample is mounted, the yield is 81%.

Procedure 12

Radium Assay in Uranium Ore Process Solutions[75]

Principle

Radium is coprecipitated with barium chloride from sulfate-free solutions. Radium is coprecipitated with lead sulfate from sulfate-containing solutions, and separated from lead by coprecipitation with barium chloride.

Procedure

The details of technique and interpretation of the assay method for a particular routine application should be determined by further experiments on actual samples. For sulfate-free solutions it will be necessary to determine whether a single $BaCl_2$ precipitation is sufficient, or whether a double precipitation is required. The correction for contaminating α activity should be determined for each type of solution by a number of parallel precipitation and emanation analyses. It may be desirable to determine more accurately the factor for converting counting rates to radium concentrations, by adding known amounts of radium to process solutions. If the techniques are standardized, the empirical determination of this factor will make a knowledge of chemical losses, self-absorption, etc., unnecessary. The rate of growth of AcX activity in the particular type of solutions to be assayed should be determined. Finally, it may be possible to simplify the assay techniques by eliminating washes, etc.

Tentative procedures for the assay of process solutions are given in detail below.

<u>Sulfate-free Solutions</u> Total time required: 25 min.

1. Measure 1 ml of the fresh solution into a 15-ml centrifuge cone.
2. Add 0.05 ml of 1.5M $BaCl_2$ solution (10 mg of Ba).
3. Add 7 ml of a cold (0°C) mixture of 6-to-1 concentrated HCl-ether mixture, stir with a platinum wire (20 gauge), keeping tube in ice bath.
4. Centrifuge 3 min at 3,000 rpm, withdraw supernatant liquid with transfer pipet, discard supernatant liquid.
5. Wash precipitate with 1 ml of ice-cold HCl-ether, centrifuge, discard supernatant liquid.
6. Repeat step 5.
7. Add 0.5 ml of 1N HNO_3 to dissolve precipitate. Using a transfer pipet, transfer the solution to a clean pyrex counting plate (2 mm thick, 4 cm in diameter) ringed with Zapon lacquer (applied with a brush in a margin 2 to 4 mm wide around the edge and allowed to dry). Rinse the centrifuge tube and pipet several times with 1N HNO_3 to obtain a complete transfer.
8. Place the counting plate on a thin asbestos sheet on a small hot plate and heat from above with an infrared heat lamp (250 watt) until bubbles begin to form and rise (2 to 3 min to drive off radon).

9. Add 5 drops of 1N H_2SO_4 and evaporate to dryness.
10. Flame the plate with a Meker burner to burn off the Zapon ring and to drive off all H_2SO_4.
11. Count the deposit immediately (within 20 min) in a standard parallel-plate α counter.
12. Calculate the radium content of the process solution as follows: Radium concentration (g/ml) = counting rate (c/m) x 10^{-12}.

Sulfate-containing Solutions Total time required: 45 min.

1. Measure 1 ml of the fresh solution into a 15-ml centrifuge cone.
2. Add 0.05 ml of 0.3M $Pb(NO_3)_2$ solution (3 mg of lead). Stir well with a platinum wire (20 gauge).
3. Add 0.2 ml of concentrated H_2SO_4, stir vigorously (final H_2SO_4 concentration 6N). Cool 2 to 3 min in ice bath.
4. Centrifuge 3 min at 3,000 rpm, withdraw supernatant liquid with transfer pipet and discard.
5. Add 1 ml of distilled water and 1 drop of 5 per cent aerosol, suspend precipitate by stirring with platinum wire, centrifuge, and remove supernatant liquid as before.
6. Repeat step 5.
7. Repeat step 5 again.

8. Carefully add 1 ml of water without stirring, centrifuge, and remove supernatant liquid (to remove aerosol).

9. Add 1.5 ml of a cold (0°C) mixture of 6-to-1 concentrated HCl-ether mixture; stir to dissolve precipitate, keeping tube in ice bath.

10. Add 0.05 ml of 0.3$\underline{M}$ $BaCl_2$ solution (2 mg of Ba); stir well.

11. Centrifuge; discard supernatant liquid.

12. Suspend precipitate in 1 ml of ice-cold HCl-ether mixture, centrifuge, and discard supernatant liquid.

13. Repeat step 12.

14. Add 0.5 ml of 1$\underline{N}$ HNO_3 to dissolve precipitate. Using a transfer pipet, transfer the solution to a clean Pyrex counting plate (2 mm thick, 4 cm in diameter) ringed with Zapon lacquer (applied with a brush in a margin 2 to 4 mm wide around the edge and allowed to dry). Rinse the centrifuge tube and pipet several times with 1$\underline{N}$ HNO_3 to obtain a complete transfer.

15. Place the counting plate on a thin asbestos sheet on a small hot plate and heat from above with an infrared heat lamp (250 watts) until bubbles begin to form and rise (2 to 3 min, to drive off radon).

16. Add 5 drops of 1$\underline{N}$ H_2SO_4 and evaporate to dryness.

17. Flame the plate with a Meker burner to burn off the Zapon ring and to drive off all H_2SO_4.

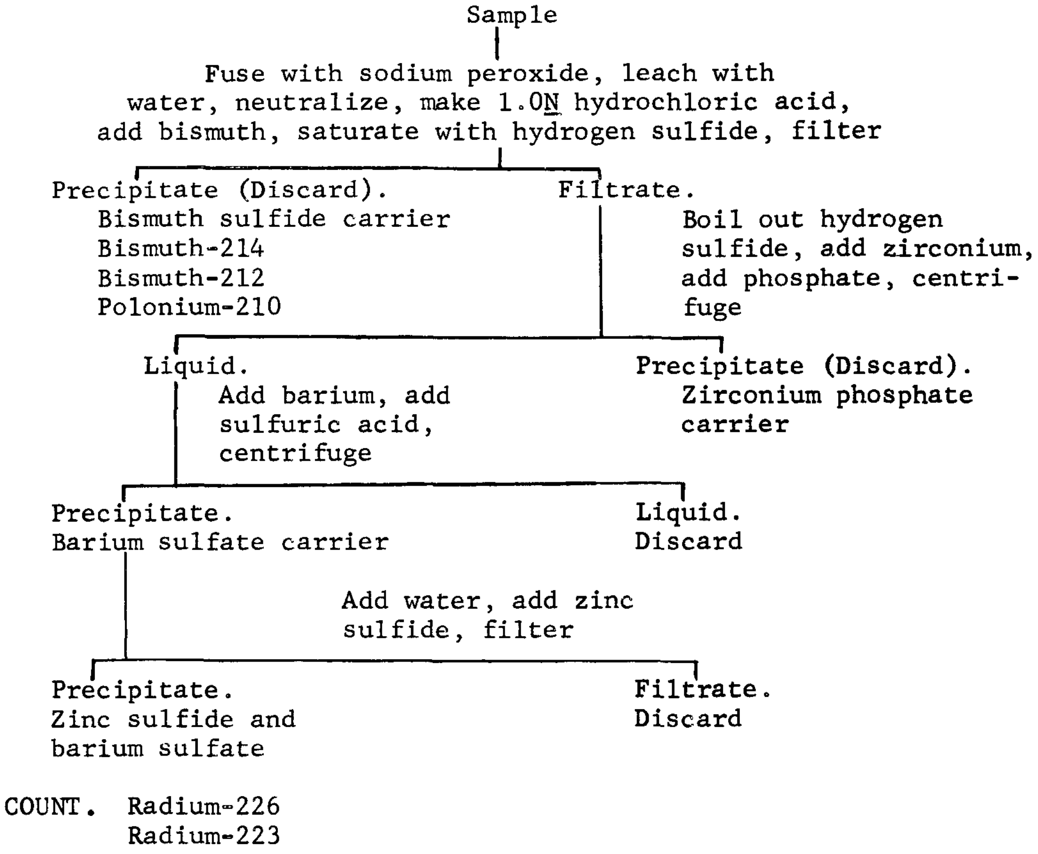
18. Count the deposit immediately (within 20 min) in a standard parallel-plate α counter.

19. Calculate the radium content of the process solution as follows: Radium concentration (g/ml) = counting rate (c/m) x 10^{-12}

Procedure 13

Determination of Radium Isotopes in Minerals[70]

Principle (Schematic Outline of Procedure)



Apparatus

Measurements are made on the radioactive precipitate mixed with zinc sulfide, using a phosphor thickness of 15 to 20 mg. per sq. cm. The active phosphor is placed in the scintillation detector directly beneath the bare photomultiplier tube and allowed to remain in the dark for at least 15 minutes before the high voltage is applied to the phototube and the counting is begun. The scintillation counter consists of a bare photomultiplier tube enclosed in a light-proof metal container, 4 inches in diameter and 10 inches high, equipped with a felt-sealed hinged door. The photomultiplier tube, with a sensitive window surface 3 inches in diameter, is coupled through a cathode follower to a conventional scaling unit.

The precipitates are filtered on 50-mm. Millipore filter membranes used with Millipore filter apparatus (Millipore Filter Corp., Watertown, Mass.). The surface of the membrane is impervious to penetration by the precipitate. An aluminum ring, 50 mm. in diameter by 3 mm. high with 0.005-gage cellophane glued to its underside, is used for the zinc sulfide-precipitate mount. Plastic cement is spread on the periphery of the underside of the ring directly on the cellophane and the precipitate and membrane are mounted by adherence to this surface. A 47-mm. ring without the cellophane protector is used to mount the bismuth sulfide-carried precipitate.

Reagents

Bismuth carrier, 0.028M bismuth chloride in 5% hydrochloric acid solution (6 mg. of bismuth per ml.).

Zirconium carrier, 0.16M zirconium chloride solution (15 mg. of zirconium per ml.).

Barium carrier, 0.146M barium chloride solution (20 mg. of barium per ml.).

0.1M sodium pyrophosphate solution.

Zinc sulfide, powder, phosphorescent grade, nonactivated.

0.05 millicurie radium-226 source solution.

National Bureau of Standards 10^{-9} gram radium-226 standard solution.

Procedure

The sample, 1 gram or less depending on total activity and ease of solution, is fused at almost red heat with 4 to 5 grams of sodium peroxide in a nickel crucible. The melt is allowed to disintegrate in water and neutralized with hydrochloric acid. The solution is diluted to 100 ml. while the acidity is adjusted to 1.0 N in hydrochloric acid. The sample should be completely in solution. If all of the silica is not taken into solution, a smaller sample should be used.

Six milligrams of bismuth carrier are added, and the solution, at about 45° C., is saturated with hydrogen sulfide. The bismuth and polonium isotopes are coprecipitated with the bismuth carrier and filtered on Millipore membranes.

The filtrate containing the uranium, protactinium, thorium, actinium, radium, and lead isotopes is made free of hydrogen sulfide by evaporation on a hot plate to a volume of approximately 80 ml. Fifteen mg. of zirconium carrier and 3 ml. of sodium pyrophosphate solution are added separately to the filtrate and the solution is boiled gently for 1 to 2 minutes while the zirconyl phosphate precipitate is forming; this precipitate carries thorium quantitatively. The hot solution is immediately centrifuged, the supernatant liquid decanted, and the precipitate is discarded. Measurements on zirconium phosphate precipitates from solutions containing 10^{-9} gram of radium-226 show that less than 0.2% of the radium is retained in the precipitate.

Twenty milligrams of barium carrier are added to the supernatant liquid. Three milliliters of dilute sulfuric acid are added to the warm solution, precipitating the radium with barium sulfate. The precipitate is allowed to settle for 15 minutes and centrifuged, and the supernatant liquid is decanted and discarded. The precipitate is rinsed from the centrifuge tube with 30 ml. of water and 2 drops of hydrochloric acid are added. Then 150 mg. of zinc sulfide are added, the slurry is mixed well, filtered, washed, mounted, and dried, and the time is recorded. The precipitate is collected as a 35-mm. diameter circle in the center of a 50-mm. membrane. Less than an hour should elapse between the zirconium phosphate separation and the barium sulfate filtration.

(Reviewer's note - For details of the efficiency determination and differential decay analysis, the reader is referred to Rosholt's original article.)

Procedure 14

Standardization of Radium Solutions by Alpha Counting[74]

Principle

Polonium-210 is removed by spontaneous electrodeposition on copper powder and radon retention is determined by differential decay analysis.

Procedure

The end of a small glass funnel is drawn to an opening of approximately 2 mm. and a small plug of glass wool is inserted. Approximately 0.2 gram of hydrogen-reduced copper powder (150 to 200 mesh) is poured into the funnel to form a column about 5 mm. high and 3 to 4 mm. in cross section. The flow rate should be about 1 drop per second when the stem is filled. The copper is washed with dilute (1:5) hydrochloric acid until it appears bright. The column is thoroughly rinsed with water and dried with alcohol and ether in a stream of air.

The stem of the funnel is filled with a dilute hydrochloric acid solution of the radium sample to be analyzed, precautions being taken against the formation of air bubbles in the stem. The funnel is not filled above the stem.

The first 2 or 3 drops of the effluent are discarded, and the remainder is collected in a small test tube or vial. The mouth of the collecting vessel is kept small to minimize evaporation. If the sample is not mounted immediately, the vessel is stoppered tightly.

Within 3 days after the copper reduction, an aliquot of the polonium-free sample (up to 0.1 ml. containing from 5 X 10^{-5} to 0.02 microgram of radium) is mounted, the mount being spread over as large an area as possible to reduce self-absorption. The sample is dried under an infrared lamp adjusted to a height of 2 inches from the sample. Zero time (the time when heating was begun) is noted.

The sample disk is counted at 4.0, 4.5, or 5.0 hours and returned to its container until 24.0 hours after zero time, when it is counted again.

The percentage increase between the two counts is computed, and the correction factor is found from Figure 12, or by direct calculation as described below. The correction factor is applied to the counts obtained at the earlier time to find the activity due to pure radium.

Calculation of correction factor The method of calculating the correction factor is best explained by an example. Suppose that the samples were counted at 4.5 and 24.0 hours and that the counting rates were 10,000 and 10,909 counts per minute, respectively. The increase in counts is 9.09%, while the increase in counts if 100% of the radon had been retained (Table IV, C) would have been

$$\frac{1.4892}{1.0922} - 1 = 36.35\%$$

Therefore, the actual radon retention is

$$\frac{9.09}{36.35} = 25\%$$

At 4.5 hours, the relative activity of the alpha-emitting daughters of radium (Table IV, A) would have been 0.0910 if 100% of the radon had been retained. But since only 25% of the radon was retained, the relative increase is only 0.0910 X 0.25 = 0.0228. In addition, if the samples were mounted immediately after the copper reduction, the radium C' which grew from unreduced radium B will not yet have decayed to insignificance (Table IV, B). Adding this small contribution, the total relative alpha activity at 4.5 hours is 0.0228 + 0.0012 + 1.0000 = 1.0240. The alpha activity directly due to radium is therefore

$$\frac{10,000}{1.0240} = 9766 \text{ counts per minute}$$

To simplify the calculation of the correction factor, a graph can be constructed relating the percentage increase in counts directly to the correction factor. For example, it has already been shown that the increase in counts (for 100% radon retention) between 4.5 and 24.0 hours is 36.35%, corresponding to a correction factor of 1.0922. Plotting per cent increase on the abscissa and correction factor on the ordinate, a straight line is drawn between the points having coordinates of (0.00, 1.0012) and (36.35, 1.0922). The correction factor can now be read directly if the increase in counts is known.

Such a plot has been made in Figure 12 for the usual case where the second set of counts is made at 24.0 hours, and similar graphs for other time periods can be easily constructed from the calculated values in Table IV.

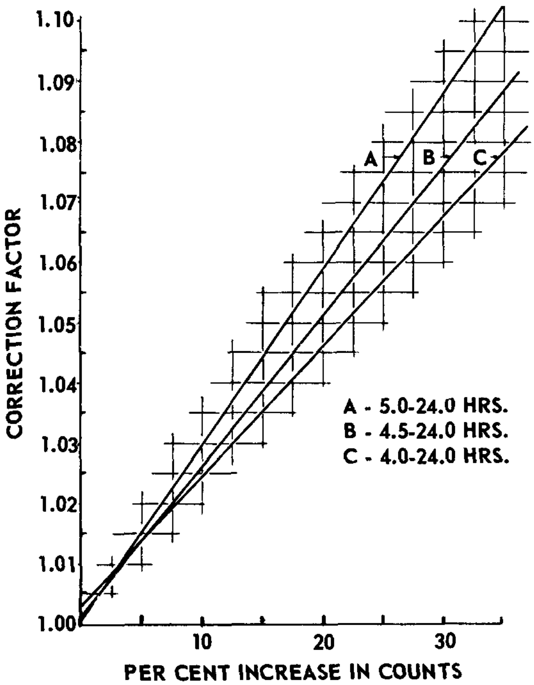


Fig. 12. Correction for growth of radium daughters.

Table IV

CALCULATED ALPHA ACTIVITY OF THE RADIUM CHAIN RELATIVE TO THAT OF PURE RADIUM

Time Hours	A	B	C	D
4.0	0.0799	0.0034	1.0833	1.0034
4.5	0.0910	0.0012	1.0922	1.0012
5.0	0.1021	0.0008	1.1029	1.0008
5.5	0.1127	0.0003	1.1130	1.0003
6.0	0.1237	0.0002	1.1239	1.0002
18.0	0.3733	0.0000	1.3733	1.0000
24.0	0.4892	0.0000	1.4892	1.0000
48.0	0.9053	0.0000	1.9053	1.0000
72.0	1.2523	0.0000	2.2523	1.0000

A. Relative alpha activity of the daughters of radium growing from initially pure radium, assuming no loss of radon.

B. Relative alpha activity of radium C', the only significant alpha-emitting daughter of radium B, after removal of all polonium, bismuth, and radon from a radium solution which was initially at 50% of equilibrium with radon and its short-lived daughters.

C. Correction factor for 100% retention of radon (=A + B + 1.0).

D. Correction factor for 0% retention of radon (=B + 1.0).

Procedure 15

Determination of Radium-226 in Process Solutions Containing Actinium-227 and Thorium-228[88]

Principle

Radium-226 is determined by precipitating radium-barium nitrate from 80 per cent nitric acid and determining the radium-226 in this precipitate. A differential decay technique is used to distinguish radium-226 from other radium isotopes.

Procedure

The solution to be analyzed is centrifuged or filtered, and a sample of the clear liquid (up to five milliliters) is transferred to a 30-milliliter beaker together with two drops of 70 per cent perchloric acid for each milliliter of sample. A magnetic stirring bar is introduced and the solution is evaporated to dryness under an infrared lamp with continuous stirring. Distilled water is added until the residue redissolves, and 10 milligrams of barium, as barium nitrate, is introduced into the solution. The mixture is stirred vigorously and an equal volume of concentrated nitric acid is added. The solution is evaporated under the infrared lamp with constant stirring until nearly dry. The sides of the beaker are washed with two milliliters of concentrated nitric acid, and the solution is evaporated to approximately one milliliter.

The solution is cooled in an ice bath for five minutes, and two milliliters of red fuming nitric acid is added slowly with constant stirring. The beaker is covered, and the precipitate is digested in the ice bath for 20 minutes.

The solution is filtered through a medium fritted disk, and the precipitate is washed three times with one milliliter of red fuming nitric acid. The filtrate and washings are discarded.

A small volumetric flask is placed under the filter, and the precipitate remaining in the original beaker is dissolved in hot distilled water. The solution is allowed to pass slowly through the filter into the volumetric flask, and the beaker and frit are washed several times with hot distilled water until the precipitate is completely redissolved.

The volumetric flask is allowed to cool, made up to volume, and set aside for five days. At some time after the fifth day, a stainless steel disk is prepared by the following technique:

> An aliquot of the barium nitrate solution (preferably not greater than 50 microliters) is mounted in discrete droplets of two microliters or less. The droplets should be so spaced that they will not run together when heated.
>
> The micropipette is rinsed with a drop of dilute nitric acid, and the disk is dried under an infrared lamp. When dry, the disk is ignited over a Meker burner and held at red heat for 60 seconds. The time of ignition is noted as T_0.

One to three days later, another aliquot is mounted in the same manner, and the time is so arranged that the ignition takes place at precisely 24, 48, or 72 hours after ignition of the first sample.

One, two, or three days after ignition of the second disk, both disks are counted in the same instrument, the time being so arranged that the first is counted just before T_0 plus D days and the second is counted immediately after the background introduced by the first sample has been determined.

The radium-226 is determined from simultaneous equations, the technique being best explained by the following example:

Sample No. 1 was prepared at 8:30 A.M., October 13, and counted at 8:25 A.M., October 15. It had 100,000 alpha counts per minute. Sample No. 2 was prepared at 8:30 A.M., October 14 and counted at 8:35 A.M., October 15. It had 90,000 alpha counts per minute.

Two simultaneous equations are now set up, using the growth factors in Table V. Since Sample No. 1 was two days old when counted, the growth factor is 1.6384, while, for Sample No. 2, the growth factor is 1.3480.

$$100{,}000 = 1.6384X + Y + Z$$

$$\underline{90{,}000 = 1.3480X + Y + Z}$$

$$X = \frac{10{,}000}{0.2904} = 34{,}435 \text{ alpha counts per minute of radium-226 on the slide}$$

(Note that Y and Z represent the counts due to radium-223 and radium-224, respectively, and are identical in both samples at any given time.)

Table V

GROWTH FACTORS FOR RADIUM-226

(70 PER CENT RADON RETENTION)

Days	Factor
1	1.3480
2	1.6384
3	1.8807
4	2.0828
5	2.2514
6	2.3920
7	2.5094

Procedure 16

Determination of Isotopic Radium[89]

Principle

Total radium is precipitated with barium carrier, dissolved, and purified by solvent extraction. The concentrations of each of the radium isotopes are determined by selective extraction of the lead and bismuth daughters at suitable times. Radium-223 is determined by counting 36-minute Pb-Bi-211, Ra-224 by counting one-hour Bi-212, and Ra-226 by counting 20-minute Bi-Po-214.

Apparatus and Reagents

A gas-flow proportional counter (Nuclear Measurements Corp., Model PCC-10A)capable of handling a 2" diameter internal sample was used. Equivalent alpha counting equipment, proportional or scintillation, can be employed. No other special equipment is necessary.

Reagents required:

1. 2-thenoyltrifluoroacetone (TTA), 0.5M in benzene
2. 8-hydroxy-quinoline, 0.1M in chloroform
3. $BaCl_2$ solution, 5 mg/ml standardized
4. $(NH_4)_2SO_4$ solution, 50% by weight
5. Ethylenediaminetetraacetic acid, disodium salt (EDTA) solution, 10% by weight.
6. Na_2CO_3 solution, 25% by weight
7. Acetate buffer solution, pH 4.6. Mix equal volumes of 1M sodium acetate and 1M acetic acid.
8. H_2SO_4, 1M
9. HNO_3, conc.

Some care should be exercised in choice of the reagents used, and in particular the sodium carbonate. If low level work is to be done they should be each examined for radium content; in some cases it has been necessary to purify the sodium carbonate before use.

Procedure

1. Adjust one liter of sample to pH 3-5. Add 2 ml of 50% $(NH_4)_2SO_4$, 20 ml of 10% EDTA, and 20 mg of barium as $BaCl_2$ solution. Stir for ten minutes; the final pH should be less than 5; if not, adjust with dilute H_2SO_4.
2. Centrifuge, collect the precipitate in a 50-ml centrifuge tube, wash, and recentrifuge.
3. To the precipitate add 20-30 ml of 25% Na_2CO_3, place the centrifuge tube in a beaker of boiling water, and heat for five to ten minutes, stirring occasionally.
4. Cool the solution, centrifuge, wash, and recentrifuge. To the $Ba(Ra)CO_3$ precipitate add 2-3 drops of concentrated nitric acid to dissolve. If the precipitate does not dissolve completely repeat step 3. Transfer the solution to a 60-ml separatory funnel using acetate buffer solution to wash out the tube, and make up to 30-40 ml.
5. Add 4 ml of TTA-benzene and extract for 5 minutes with not too vigorous shaking. Allow the layers to separate and transfer the aqueous layer to another separatory funnel. Note the time of separation. Discard the organic layer.
6. Wait 31 minutes, add 4 ml of TTA-benzene to the aqueous solution and extract for five minutes, making 36 minutes in all. Separate the layers, transferring the aqueous to a centrifuge tube; again, note time of separation.
7. Mount the organic layer (an aliquot may be used with samples

of high activity) on a two-inch planchet, dry, flame and count for alpha activity. Follow the decay in the count rate for 2-3 hours or until constant activity is attained. Plot the count rate *versus* time, with zero taken as the time of the second separation (Step 6). Extrapolate the decay curve back to this zero time and determine the contribution of 36-minute activity. (Note 1).

Note 1. The decay curve should follow the 36-minute half life of Pb-211. If counting is started less than about ten minutes after separation (Step 6), a slight curvature may be noticed due to bismuth-211 ingrowth, but generally as both the bismuth and the lead are extracted, such curvature does not appear. The zero time alpha activity of the bismuth (in equilibrium with the lead) will be 0.532 times the initial Ra-223 activity.

8. To the aqueous layer from step 6 add several drops of dilute H_2SO_4 to reprecipitate $Ba(Ra)SO_4$.
9. Centrifuge, wash, recentrifuge, and discard solution.
10. Add 20-30 ml of 25% Na_2CO_3 and heat as in Step 3; centrifuge, wash and recentrifuge.
11. Wait for 21 hours from the separation time in Step 6. This will give an ingrowth of Bi-212 to about 65% of the initial radium-224 activity.
12. Discard the supernatant solution, dissolve the precipitate in a few drops of concentrated HNO_3, transfer to a separatory funnel, and adjust to pH 4 with acetate buffer.

Extract with 4 ml of 0.1M 8-hydroxyquoinoline in $CHCl_3$.

13. Separate the layers and note the time of separation; this will be the zero time for the Bi-212 decay plot. Draw off the organic layer, mount, dry, ignite, and alpha count. Follow the decay in activity for 3-4 hours. Plot as before, and determine the activity at zero time (Note 2).

    Note 2. The Bi-212 activity after 21 hours ingrowth will be 0.656 times the initial Ra-224 activity.

14. Transfer the aqueous layer from Step 13 to a centrifuge tube; repeat steps 8-10.

15. Wait a suitable length of time, say 2-6 days, for ingrowth of Rn-222 and its daughters.

16. Centrifuge, and discard the supernatant solution.

17. Dissolve the precipitate in a few drops of HNO_3, buffer, and extract as in Step 12.

18. Separate the layers, noting the time of separation as the zero for the Bi-214 plot. Planchet the organic layer, ignite, and count for alpha activity. Follow the decay curve for 2-3 hours and determine the initial Bi-214 activity as before. Two contributors to the activity may be noted - 20 minute Bi-214 and one-hour Bi-212. From the initial Bi-214 activity the net Ra-226 activity may be calculated, but the actual numerical values used will depend on the number of days taken for ingrowth.

19. Place the aqueous layer in a separatory funnel and repeat the TTA extraction of step 5 to remove residual radium

daughters. Discard the organic layer.

20. Transfer to a centrifuge tube; add a few drops of dilute H_2SO_4 to precipitate $Ba(Ra)SO_4$. Centrifuge, wash and recentrifuge.

21. Transfer the precipitate to a planchet, ignite, weigh, and count for alpha activity. The total recovery of the method can be checked by the weight of the barium sulfate on the final planchet. The total radium activity determined here will also contain contributions from the short half-lived daughters of both Ra-223 and Ra-224, the amount depending on the time between the final precipitation and counting. It is best to wait at least two hours before counting to allow for ingrowth. (Note 3)

Note 3. The "total radium" alpha activity determined will comprise not only the activity of the radium isotopes but their shorter lived daughters as well. For a two hour waiting period after separation (Step 19), negligible activity will come from Ra-226 decay products, but almost complete ingrowth of Ra-223 daughters will occur (4 alphas total). Only partial ingrowth of the Ra-224 daughters will have taken place; the Pb-212 will not be in equilibrium so that only slightly more than three alphas will be observed per Ra-224 decay. The activity determined for "total radium" will therefore be the Ra-226 activity plus 4 times the Ra-223 activity plus 3+ times the Ra-224 activity. For waiting periods of other than two hours the ratios will be different.

(Reviewer's note: The detailed report shows that a substantial fraction of actinium-227 is carried through the procedure. Although Ac^{227} is primarily a beta-emitter, the growth of its alpha-active decay products is rapid and may affect the radium-224 and radium-226 results, depending on the relative amounts of the radium isotopes and the length of time between separations.)

Procedure 17

Determination of Isotopic Radium[89]

(Reviewer's note: This procedure is included as an appendix to, and should be read in conjunction with, Procedure 16.)

Principle

The following procedure for isotopic radium depends upon ion exchange separation of lead, bismuth, and radium. It has been found to be somewhat slower than the solvent extraction procedure, and is more difficult in manipulation. Although never extended to the direct determination of Ra-226, it should be capable of such extension. Some improvement of the method is perhaps possible; for instance, the reprecipitation and metathesis of Steps 8-12 could perhaps be eliminated if care were taken to insure against radon loss.

Procedure

1. To a suitable aliquot of sample add 10 mg of barium carrier (Pb carrier may be used also), excess $SO_4^=$, stir for ten minutes, and centrifuge. Wash with 10 ml of water and discard wash.

2. To the precipitate add 10 mg of bismuth carrier, 2 ml of Versene-100 (EDTA), and 5 ml of 2M NaOH. Heat to dissolve barium, centrifuge, and discard $Bi(OH)_3$ precipitate.

3. Add to the solution 5 ml of glacial acetic acid, and 2 ml of 10% $(NH_4)_2SO_4$ (or a few drops of dilute H_2SO_4).

4. Centrifuge the precipitate and wash with water, discarding the wash.

5. Add to the precipitate 15 ml of 25% Na_2CO_3, and stir while heating in a water bath for 2 minutes.

6. Centrifuge the precipitate, wash, and discard the washings.

7. Dissolve the $Ba(Ra)CO_3$ precipitate in 3 ml of 1.8M HCl and add to an anion exchange column (Dowex 1-X8, 1 cm in dia. by 18 cm long). Elute with 30 ml of 1.8M HCl at 5-8 ml/min.

8. Add 5 ml of 10% $(NH_4)_2SO_4$ to eluates to precipitate $Ba(Ra)SO_4$.

9. Centrifuge, wash, and recentrifuge again.

10. Repeat steps 5 and 6 to convert the precipitate to the carbonate. Note the time of the conversion.

11. To the precipitate add 10 ml of 25% Na_2CO_3, stir for 2

minutes, and centrifuge. Wash and recentrifuge, saving the precipitate.

12. Add to the precipitate 5 mg of lead carrier, and 10 mg of bismuth carrier.
13. Allow the precipitate to stand 36 minutes from the time noted in step 10.
14. At the end of the ingrowth period add 2 ml of 4<u>M</u> HCl to dissolve the precipitate.
15. Add to an anion column as in step 7 and elute the barium and radium with 30 ml of 1.8<u>M</u> HCl, the lead with 60 ml of 8<u>M</u> HCl, and the bismuth with 120 ml of 1<u>M</u> H_2SO_4, in that order.
16. Precipitate the Ba(Ra) fraction with $(NH_4)_2SO_4$.
17. Precipitate the Pb by neutralizing and adding $CrO_4^=$.
18. Precipitate the bismuth by addition of $PO_4^≡$.
19. Centrifuge all the precipitates, wash with water, recentrifuge, mount on weighed planchets, and dry.
20. Alpha count, and in the case of the lead and bismuth follow the decay.
21. Weigh the planchets to get chemical yields.

Procedure 18

Determination of Radium-228 in Thorium Solutions[90]

Principle

Thorium is removed by extraction with ITA followed by extraction of Ac^{228}, which is purified by lead sulfide precipitation and coprecipitated with lanthanum oxalate. Radium-228 is determined by extrapolation of the Ac^{228} decay curve.

Procedure

1. Extraction of thorium into 0.25 molar TTA
    (a) The sample to be analyzed was evaporated, if necessary, until the concentration of thorium was less than 30 grams of thorium per liter.
    (b) Five milligrams of lanthanum and ten milligrams of lead carrier were added to the solution to be analyzed. (The carriers were in the nitrate form)
    (c) The pH of the solution was adjusted with one normal sodium hydroxide to a value of 1.7 ± 0.1.
    (d) The solution was contacted for five minutes with 50 milliliters of 0.25 molar ITA dissolved in benzene.
    (e) The aqueous phase was removed and the pH adjusted to 1.7 again with one normal sodium hydroxide.
    (f) The TTA extraction was repeated, with fresh TTA, until no change in pH was observed during the course of one extraction. The thorium was then completely removed.

2. Extraction of carriers, actinium and other daughter products

   (a) Three or four drops of indicator (a mixture of bromocresol green and chlorophenol red) were added and one normal base was added until the indicator turned blue-green.

   (b) The aqueous phase was extracted for five minutes with 50 milliliters of 0.25 molar TTA.

   (c) After about one minute of extraction, the agitation was stopped and the phases were allowed to separate. One normal base was then added until the blue-green color was restored. This procedure was repeated several times during the agitation period to insure that the aqueous phase had a pH of above six at the end of the five-minute period. The time when all these extractions were done was noted.

   (d) The above procedure was repeated three times. After the first extraction, however, the pH did not change a great deal as the various extractions took place.

   (e) The 200 milliliters of actinium-bearing TTA were stirred for several minutes with wash water at a pH of seven. This reduced the mechanical carry-over of radium-228.

3. Stripping of daughter products into 0.1 normal nitric acid
   (a) Four 50-milliliter portions of 0.1 normal nitric acid were stirred for five minutes each with the TTA solution from Step 2. The carriers, actinium, and lead isotopes were then in the aqueous phase.
   (b) The acid solution was then heated to drive off any benzene present.
4. Sample preparation
   (a) The aqueous phase from Step 3 was saturated with hydrogen sulfide gas. A black precipitate of lead sulfide formed.
   (b) One hundred milliliters of the aqueous phase were placed in centrifuge tubes and centrifuged for 12 minutes. This packed the sulfide precipitate into the bottom of the centrifuge tube. The centrifugate was poured, with care, into a beaker in order not to disturb the packed precipitate. The second 100 milliliters were centrifuged in a like manner.
   (c) The centrifugate was boiled to remove any unreacted hydrogen sulfide gas and cooled to room temperature.
   (d) Ten milligrams of oxalic acid and several drops of indicator were added to the cooled solution.

(e) One normal sodium hydroxide was added until the indicator just turned blue-green. Lanthanum oxalate precipitated.

(f) The precipitate was filtered through three pieces of Schleicher and Schuell 589 Red Ribbon filter paper. The diameter of the filter circles was one and one-eighth inches. The filtration was accomplished using a sintered glass filter disc and a glass chimney.

(g) The three filter papers were mounted on one and one-quarter inch diameter aluminum planchets and were covered with cellophane tape.

(h) The filtrate from the lanthanum oxalate filtration was made slightly acid with nitric acid and more lanthanum and oxalic acid were added. Sodium hydroxide was then added and more lanthanum oxalate was precipitated to insure complete removal of the actinium. This filter paper was also mounted on an aluminum planchet.

5. Counting procedure

(The beta particles were counted using a mica window tube and conventional scaler.)

(a) The four planchets were counted to determine the decay curve.

(b) The decay curve was plotted on semi-log paper and extrapolated back to the time noted at the end of the first actinium extraction. This was the time that the actinium was assumed to be separated from the radium-228.

The decay curve is an important part of the analytical procedure. It is advisable to plot the decay curve for several days to ascertain if any long-lived emitters are present. This was not necessary when high-activity samples were being analyzed, but the procedure was necessary when analyzing extract samples since the amount of radium-228 present was small.

If an aqueous solution had been contacted with tributyl phosphate (TBP), it was allowed to stand for 24 hours before the radium-228 analysis. Since the actinium has a half-life of 6.13 hours, the 24 hours assured the attainment of radioactive equilibrium before the analysis was started.

Due to contamination the slope of the actinium decay curve was rarely 6.13 hours. Most observed half-lives were from 6.2 to 6.3 hours. The equilibrium activity noted, however, did not vary significantly with the increased half-life.

A slightly different technique was used to analyze organic extract phases for radium-228. A known amount of the extract phase was stripped four times with distilled water to remove any thorium and radium-228 present. The fifth strip was tested with ammonium hydroxide to insure that all the thorium had been removed. The distilled water strip solution was then evaporated to reduce the volume. Since the solution then usually contained more than one gram of thorium, the following procedure was used for the thorium extraction.

1. Extraction of thorium into 0.75 molar TTA
    - (a) The carriers were added as in the previous analysis.
    - (b) The pH of the aqueous was adjusted with base to 1.7 ± 0.1.
    - (c) The solution was extracted for five minutes with 0.75 molar TTA.
    - (d) At the end of the extraction the aqueous phase was removed and the pH was adjusted to the value of 1.7. This aqueous phase was then placed in contact with the TTA used in Step (c) above.
    - (e) Step (d) was repeated until no pH change was observed over the course of one extraction.

      The TTA was then saturated with thorium. Fifty milliliters of fresh 0.75 molar TTA was then used and the same technique repeated. If the sample contained about three grams of thorium, only two batches of TTA were found to be necessary.

Procedure 19

Determination of Radium in Residues from Pitchblende Processing[93]

Principle

Radium is brought into solution by alkaline fusion and de-emanated by bubbling in a hot water bath.

Procedure

Weigh a five g sample into a 30 ml platinum crucible. Add two ml of 50% H_2SO_4, and then fill two-thirds full with 48% HF. Heat the crucible gently to permit evaporation without any bubbling. When the liquid remaining is about two ml cool the crucible, refill with HF, and resume heating. Do this once more. Most of the silica has now been removed. Now suspend the residue in water in the crucible, and treat with hot, saturated ammonium acetate containing a little $(NH_4)_2SO_4$. Stir, and decant through a Whatman No. 42 filter paper. The filtrate is discarded. Treat the residue again with hot ammonium acetate and finally with water. Most of the lead has now been removed. The filter paper is placed in the platinum crucible, charred, and ignited. The residue is again treated with H_2SO_4 and HF, as above. Cool. Pour the sulfuric acid-containing residue into water, and scrub out the platinum crucible. Filter, and ignite again as described above. This residue contains all of the barium and radium as sulfates.

Fuse the weighed residue with ten times its weight of anhydrous Na_2CO_3. While the crucible is hot, remove the cover and place the cover in a beaker containing 50 ml water. Remove the crucible from the heat, and tilt and rotate it to spread the melt over the sides of the crucible. Place the crucible in the water containing the crucible cover. Heat the beaker, and scrub the crucible to promote solution of the melt. Decant the liquid through a Whatman No. 42 filter paper. Continue this process until all the melt has disintegrated. Wash thoroughly with hot one per cent Na_2CO_3 solution to ensure complete removal of sulfates. The residue contains all of the radium and barium as carbonates. Dissolve the carbonates in dilute HNO_3.

Residual lead must now be removed Precipitate the lead, barium and radium by addition of H_2SO_4 to the above HNO_3 solution. Allow the precipitate to stand overnight; filter on Whatman No. 42 filter paper, and wash five times with hot water. Discard filtrate. Now pour over the filter 100 ml of hot, saturated, ammonium acetate solution containing one % $(NH_4)_2SO_4$. This dissolves the residual lead. Wash the paper with hot water. Place the paper in the original platinum crucible, char, ignite, and fuse again with Na_2CO_3. Treat the fusion mixture as before, including final solution in HNO_3.

<u>Preparation for Alpha Counting</u> Transfer the HNO_3 solution of barium and radium to a small volumetric flask; dilute to the graduation mark; and mix thoroughly. Pipette 10 ml of this solution into a 15 ml centrifuge tube or equivalent-size test tube. Fit a two-hole rubber stopper that fits the test tube

with an inlet capillary tube reaching to the bottom of the test tube and an exit tube for applying suction.

Now place the tube containing the sample and stopper in a thermostatic bath held at 85°C. Apply suction to the exit tube to bubble air slowly through the solution. Continue this aeration for a minimum of five hours. Overnight aeration does no harm. Then transfer the solution to a ten ml volumetric flask. Wash the tube, capillary, and stopper, and add the washings to the flask. Dilute to the graduation mark, and mix well. Transfer ten lambda or more of the solution to a counting slide, and dry under a heat lamp. Alpha counts are made on a suitable instrument whose geometry is known.

Procedure 20

Estimation of the Isotopic Composition of Separated Radium Samples[73]

Principle

Radium-223, radium-224, and radium-228 are determined by the separation and radioassay of their respective daughters, lead-211, lead-212, and actinium-228. Radium-226 is determined by difference.

Reagents

Radium nitrate solution. A pure solution of radium nitrate is prepared, as described in Procedure 11. Commencing with a 500-ml sample, the pure solution is obtained in 10 ml of dilute nitric acid.

Di(2-ethylhexyl)phosphoric acid (EHPA; Union Carbide Chemical Co., mono-ester free), 1.5*M* in n-heptane. After dilution with an equal volume of n-heptane, the EHPA should be purified by washing, in order, with an equal volume of 1*M* nitric acid, with an equal volume of saturated ammonium carbonate solution, with an equal volume of 3*M* nitric acid, and then twice, with an equal volume of water. To verify the concentration of EHPA, titrate in methanol with sodium hydroxide to a phenolphthalein end point.

Aliquat 336, methyltricaprylylammonium chloride, 30 volume % in benzene, is washed twice with an equal volume of 1.5*M* hydrobromic acid prior to use.

Radium-223

The determination of radium-223 is based upon the extraction, into dithizone, of the daughter activity, 36.1-minute lead-211. Before making this separation, 3 hours must elapse after the separation of lead from radium. This period is sufficient for ingrowth of lead-211. Interference from the ingrowth of lead-214 can be minimized by boiling the solution during the 3-hour period. This treatment will volatilize the 3.8-day radon-222 precursor of lead-214. The half life of the radon-219 precursor of lead-211 is short, and experimentation has proved that radon-219 decays before it is volatilized from the solution. If appreciable radium-224 is present, a correction must be made for the presence of 10.6-hour lead-212, the daughter of radium-224. This correction is easily made by decay measurement of the separated lead activity.

Procedure

Add an aliquot of the 10-ml sample of radium nitrate to a separatory funnel 3 hours after the separation of carrier lead from radium. Add 1 ml of 2.5% aqueous ascorbic acid solution, 1 drop of 1% phenolphthalein indicator solution, and neutralize with 6$\underline{M}$ ammonia and then add 2 drops in excess. Add 5 ml of 0.01% (w./v.) dithizone in chloroform, and extract for 2 minutes. Draw off the organic phase into a second funnel containing 10 ml of 1$\underline{M}$ ammonium nitrate solution, adjusted to pH 9. Wash the aqueous phase with 2 ml of chloroform and add to the second funnel.

Extract with a second 5-ml portion of dithizone. At the end of the extraction, start a stop watch. Add the dithizone extract to the second funnel. Wash the aqueous phase, as before, and add the wash solution to the second funnel.

Shake the second funnel for 30 seconds and withdraw the organic phase into a 40 ml centrifuge tube. Wash the aqueous phase twice with 2-ml portions of chloroform and add the wash solutions to the centrifuge tube. Place the centrifuge tube immediately into a boiling water bath and carefully evaporate the chloroform to dryness.

After evaporation, add 3 ml of concentrated nitric acid and evaporate to 1 ml. Mount the solution on a 2-inch diameter stainless steel planchet. Bake the planchet for 1 minute to destroy organic material.

Count the sample in an α-counter. Note the time on the stop watch when the count commences and count for exactly 20 minutes. Four hours later, count again and correct the initial count for any lead-212 present.

To compute the concentration of radium-223 present in the sample, note the interval between the time the stop watch was started and the instant the counting commenced. This interval must be known to correct for lead-211 decay during processing and will vary from 20 to 30 minutes. Since the lead-211 decays during counting, this decay must be considered. For a 20-minute counting period, the average count rate must be multiplied by 1.12 to correct for this decay. The concentration of radium-223 is computed using the equation given below.

$$\text{Radium-223} = \frac{1.12A}{0.5(0.95)^2 BCG} \text{ X d.p.m./liter}$$

A = average lead-211 count rate for 20-minute count, in cpm

B = fraction of 10-ml radium-bearing solution taken for analysis

C = correction factor for lead-211 decay during processing

G = counter geometry

The two 0.95 factors correct for the radium yield by the radium separation procedure and the lead yield for the procedure described. The 0.5 factor refers to the volume, in liters, of the initial sample taken for radium analysis.

Radium-224

Radium-224 is a daughter product of natural thorium and, hence, will be found only in the effluents of those mills treating thorium-bearing ores.

The separation procedure is chemically identical to that used for radium-223 determination, and the radium-224 daughter, 10.6-hour lead-212 is extracted. The separated radium sample must be aged for 16 to 24 hours for lead-212 ingrowth, and ingrowth is measured from the time that the 10-ml radium nitrate solution is prepared. Also, after chemical separation of lead-212, the sample must be allowed to age for 3.5 hours before counting so that any lead-211 and lead-214 present may decay.

Procedure

At a time not less than 16 hours or more than 24 hours after preparation of the pure radium nitrate solution, take an aliquot of the solution, and separate lead using the procedure described for radium-223. After 3.5 hours have elapsed, as noted on the stop watch, alpha count the sample.

From the observed count rate, the concentration of radium-224 can be calculated in a manner similar to that used for radium-

223. No correction need be made for decay during counting. The count rate must be corrected for decay during the 3.5-hour wait for decay of short-lived nuclides. Finally, the count rate must be corrected for ingrowth of lead-212 and decay of radium-224. Values for this correction factor as a function of ingrowth time are given below:

Elapsed Time, Hours	Ingrowth Factor
16	0.594
17	0.609
18	0.625
19	0.640
20	0.654
21	0.669
22	0.680
23	0.689
24	0.699

Radium-226

Radium-226 is determined by difference. The basic radium procedure (Procedure 11) provides total radiation for radium-226, radium-223 and three daughters, and radium-224 and two daughters. To determine radium-226, subtract from the gross alpha determination four times the radium-223 activity and three times the radium-224 activity.

Radium-228

Radium-228, a β emitter, will be found only in effluents from mills treating ores containing natural thorium. The determination of radium-228 in the presence of α-emitting nuclides is difficult because of its weakly energetic β emission. However, radium-228 decays into 6.13-hour actinium-228, and the procedure for radium-228 analysis involves the separation and counting of actinium-228.

Contamination of the purified radium solution by actinium-227 is eliminated by adding lanthanum holdback carrier, 0.28 gram of lanthanum per liter, to the effluent sample prior to lead sulfate precipitation. This is done only if a radium-228 analysis is to be performed. Purification of actinium from radium, lead, and bismuth is accomplished by solvent extraction. Actinium is separated from radium by extraction into EHPA. The actinium is stripped from EHPA, along with lead and bismuth, with dilute hydrobromic acid, and the bromide complexes of lead and bismuth are extracted into Aliquat 336.

Procedure

After preparation of the radium nitrate solution, age the solution for at least 36 hours for actinium-228 ingrowth. After aging, take an aliquot of the solution and evaporate just to dryness. Add 1 ml of 1M nitric acid, warm gently, and transfer to a separatory funnel with 9 ml of water. Extract for 2 minutes with 25 ml of EHPA, and discard the aqueous phase.

Start a stop watch at the end of the extraction. Wash the EHPA three times by shaking for 2 minutes with 5-ml portions of 0.10M nitric acid, and discard wash solutions.

Strip the actinium from the EHPA by shaking for 2 minutes with two 10-ml portions of 1.5M hydrobromic acid. Combine the strip solutions in a second separatory funnel containing 25 ml of Aliquat 336. Discard the EHPA. Extract the lead and bismuth by shaking for 2 minutes and draw off the aqueous phase into a beaker. Wash the solvent with 5 ml of 1.5M hydrobromic acid and add the wash solution to the beaker.

Evaporate the solution to dryness and bake for 15 minutes on a high temperature hot plate to destroy organic matter. Dissolve the actinium in hot concentrated nitric acid. Transfer the solution to a 2-inch diameter stainless steel planchet and evaporate the acid under a heat lamp. Bake the planchet on a hot plate and then count in a β counter. Note time on the stop watch when the count begins.

The actinium yield is 86%, including chemical and self-absorption losses. The radium-228 concentration can be computed from the count rate, instrument geometry, aliquot of radium nitrate taken, actinium yield, radium yield, and decay of actinium during processing, which is computed from the time noted on the stop watch.

Procedure 21

Determination of Radium in Water[100]

Principle

Radium is coprecipitated with barium sulfate, filtered through a molecular filter membrane, and counted after an aging period.

Reagents

Standard Radium Solution A National Bureau of Standards radium-226 gamma-ray standard, containing 1.0×10^{-7} gram of radium, is broken under approximately a liter of distilled water, and the solution is transferred to a 2-liter volumetric flask. The broken ampoule is leached with 50 ml of concentrated hydrochloric acid and washed with distilled water; the leach and washings are added to the original solution. Dilution to 2 liters provides a stock solution containing 5×10^{-11} gram per ml of radium. A working standard is prepared by diluting 10 ml of the stock solution plus 10 ml of concentrated hydrochloric acid to 500 ml. The usual precautions required when handling radioactive alpha emitters must be observed to prevent the contamination of personnel and equipment.

Barium Carrier Solution Two and a half grams of reagent grade barium chloride dihydrate are dissolved in 1 liter of hot distilled water; the solution is cooled and filtered.

Ammonium Sulfate Solution Four hundred grams of reagent grade ammonium sulfate are dissolved in 1 liter of hot distilled water; the solution is cooled and filtered.

Sulfuric Acid Wash Solution Concentrated sulfuric acid is diluted 1 to 200; 0.15 gram of Aerosol OT, 100% (American Cyanamid Co.) is added for each liter of solution.

Procedure

Water samples containing less than 350 mg of calcium are diluted to 1 liter in 2-liter beakers and the acidity of each is adjusted to approximately pH 3 with hydrochloric acid. A 1-liter distilled water blank, and two standards consisting of 1 ml and 5 ml of the standard radium solution in 1 liter of distilled water are prepared with each set of samples. The solutions are heated to almost boiling, and 3 ml of the barium chloride carrier is added to each. While stirring vigorously, 15 ml of the ammonium sulfate solution is added. Stirring is continued intermittently for several minutes or until the barium sulfate precipitate begins to form. The precipitates are allowed to digest at room temperature for at least 4 hours. The barium sulfate precipitates are collected quantitatively on black 47-mm hydrosol-assay molecular filter membranes (available from the Millipore Corp., Watertown, Mass.) and washed with the sulfuric acid wash solution. Use of the black filter permits the analyst to determine when the precipitate is distributed evenly.

When the filters are sufficiently dry, they are cemented to nutrient pads supplied with each filter to prevent curling. The precipitate is allowed to age 10 to 12 days; this permits the growth of short-lived daughter activities to about 90% of equilibrium, thus increasing the counting rate The activity on the filter disks is measured with an alpha-scintillation counter, and the radium content of the sample is determined by comparison with the standards. Amounts of radium as low as 0.1μμc can be detected in this manner by using 1-hour counting times.

Procedure 22

Determination of Radium in Residues[72]

Principle

The sample is solubilized with a mixture of hydrofluoric and phosphoric acids. Radium is coprecipitated with barium chloride from cold 6:1 HCl-ether.

Reagents

Orthophosphoric acid, 85%, reagent grade

Hydrofluoric acid, 48%, reagent grade

Hydrochloric acid-ether solution, 6 volumes of 12 N hydrochloric acid and 1 volume of ethyl ether

Barium chloride solution, 1.5 M

Procedure

Up to 0.5 gram of the sample is accurately weighed and transferred to a 30-ml. platinum crucible. Approximately 10 ml. of 85% orthophosphoric acid and 3 to 5 ml. of 48% hydrofluoric acid are added, and the crucible is heated gradually so that gentle boiling of the contents is maintained. When silica and most of the excess hydrofluoric acid have been volatilized (volume of the residual charge about 7 ml.), the mixture is gradually brought to a dull red heat and maintained at this temperature for 15 to 30 minutes, or until a clear viscous, fuming liquid is obtained. The cooled glassy melt is dissolved in about 50 ml. of water and the solution is diluted to some convenient volume - i.e., so that 1 ml. will contain 10^{-10} to 10^{-8} gram of radium.

A 1-ml. aliquot of this solution is transferred to a 15-ml. graduated centrifuge tube, and about 0.05 ml. of 1.5 M barium chloride is added (equivalent to about 10 mg. of barium). If the aliquot taken for analysis contains more than a few milligrams of barium, proportionately less 1.5 M barium chloride should be added. Then 7 ml. of cold (0°C.) 6 to 1 hydrochloric acid-ether is added, the mixture is stirred, and the precipitated barium-radium chlorides (monohydrates) are handled as described by Ames et al (Procedure 12)[75].

The alpha activity of the barium-radium mixture may conveniently be determined in a parallel plate counter, a methane-argon proportional counter, or a scintillation counter.

Procedure 23

Microdetermination of Radium in Solution by Means of Nuclear Photographic Emulsion[108]

Principle

The number of four-branched stars formed in a nuclear emulsion by radium and its short-lived descendants is counted. The diffusion of radon is prevented by operating at a low temperature.

Procedure

For this determination, we use the method of the photographic plate, which permits the recording of each individual ionizing particle and the integration of the alpha emissions over a period of time. For an absolute determination, it is necessary to introduce into the emulsion an accurately known volume of the active solution and to record all the disintegrations in the solid angle 4π. We therefore deposit on the plate calibrated drops which we then cover with emulsion; retrodiffusion is thus avoided as well as the self-absorption of the particles. Upon examination, one counts only the alpha particles of radium and its short-lived descendants (Rn, RaA, RaC') which form four-branched stars, and not the simple tracks (radium alphas). The probability of formation of such stars is a function of exposure time and of the half-life of the radioelement in question. The number of these four-branched stars thus gives directly the concentration of the solution.

However, it is well known that radon diffuses in the emulsion and that in some cases, the four-branched star is thus found replaced by a single track and a three-branched star which might even not be formed if the radon escaped from the emulsion. The ratio of the number of four-branched stars measured to the number which would have been produced if radon diffusion had not occurred cannot yet be accurately determined.

We have tried to make this ratio equal to unity, that is, to completely suppress the diffusion by lowering the temperature. A problem arose in that the emulsion tended to separate from its support when the plate was cooled to a very low temperature. This was solved by spreading the emulsion on a cellulose nitrate support. The plates were thus preserved without cracking at very low temperatures, but their sensitivity to ionizing particles was reduced. We therefore used more sensitive plates, such as G5, rather than K2, which is customarily used for the detection of alpha radiation. A temperature of -85°C was adopted because it is readily obtained with a mixture of dry ice and acetone and because this temperature is low enough to stop the diffusion of radon.

The ratio of the number of three-branched stars to four-branched stars is less than one per cent and we attribute this to the formation of radon before the deposition of the droplets. On the other hand, the theoretical percentage of four-branched star formation and of alpha tracks from radium has been found in good agreement with the measured percentage.

Procedure 24

Leaching of Uranium and Radium from Ores[109]

Principle

A uranium ore is leached with ferric chloride solution at elevated temperature, and radium is separated by precipitation of uranyl carbonate.

Procedure

300 grams of a highly siliceous uranium ore which analyzed 2.7 percent in U_3O_8 was dry crushed to pass 65 mesh. Besides the uranium, which was present mainly in the form of such uranium minerals as torbermite, pitchblende and/or uraninite and their alteration products, the uranium ore contained small percentages of such base metals as cobalt, nickel oxides and about five-tenths of a percent each of copper, lead and manganese oxides.

624 cc. of an aqueous solution of $FeCl_3.6H_2O$ prepared by mixing 60 grams of $FeCl_3.6H_2O$ with 600 grams of water was slowly added to the 300 grams of crushed ore making approximately two parts by weight of the solution to one part by weight of the ore. The leaching solution was then heated to 85°C. After six hours, the dilution was increased to three parts by weight of solution to one part by weight of ore by the addition of water. The solution was heated at 85°C. for eighteen more hours during which time sufficient water evaporated to bring the final dilution to two parts by weight of solution to one part by weight of ore and the solution was then filtered. The pH was noted to be approximately 2 at end of the leach. An analysis of a small portion of the filtrate showed that the ferric chloride leach had extracted

95.3 percent of the uranium and 84.8 percent of the radium as well as 88 percent of the cobalt, 19 percent of the nickel, 28 percent of the lead and 25 percent of the copper originally present in the ore. The analysis also showed that very little ferrous iron was present in the filtrate after the ferric chloride leach indicating the regeneration of a good part of the ferrous iron to ferric iron during this leaching operation.

17.33 grams of finely ground calcium carbonate was added to the filtrate to precipitate the ferric iron and some of the other base metals at a pH less than 4.7 and the solution was filtered to remove the precipitate. This precipitate containing the ferric iron, 5.1 percent of the extracted radium values and twenty percent of the extracted uranium values may be recycled for a further ferric chloride leaching.

8.73 grams of finely divided barium carbonate was added as a slurry to the filtrate from the preceding operation to precipitate the uranium from the solution as granular, free settling $UO_2CO_3.H_2O$. When the precipitation was complete at a maximum pH of approximately 5.8 - 6.0 the solution was filtered and the precipitate removed. It is preferable to make this precipitation in such a manner as to assure complete utilization of $BaCO_3$ which otherwise would contaminate the $UO_2CO_3.H_2O$ precipitate. This is best accomplished by step-precipitation whereby a given volume of the purified leaching solution heated preferably above 50°C. is agitated in the primary stoichiometric requirement of the uranium in solution until all the barium carbonate is consumed. The high grade $UO_2CO_3.H_2O$ precipitate is filtered and washed. The solution from this filtration is then agitated, either warm or cold, with slightly more than the stoichiometric requirement of $BaCO_3$, whereby additional and complete precipitation of uranium is assured, and the solution from this step passes to the subsequent procedure for radium recovery. The uranyl carbonate of this second step, after filtration or simple thickening is passed to the primary step of uranium precipitation. An analysis of a portion of the precipitate and of the filtrate of the barium carbonate precipitation showed that the precipitate contained eighty percent of the uranium and fifteen percent of the radium extracted from the ore. This uranium precipitation with barium carbonate is best completed at a pH of approximately 6 or less at which acidity radium and most of the other base metals such as ferrous iron, nickel and cobalt remain in solution.

To recover the radium in the filtrate from the uranyl carbonate precipitation step sufficient H_2SO_4 was added to the filtered solution to bring the pH to about 2.5 and to precipitate the radium from the filtrate as mixed barium and radium sulfate. This precipitation was considered complete when free H_2SO_4 was found in the solution; and an analysis of the precipitate and filtrate showed that this precipitation recovered approximately 80 percent of the radium extracted from the ore.

Procedure 25

Separation of Radium from Calcium, Strontium, and Barium[91]

Principle

Radium is eluted from a cation exchanger with EDTA at a controlled pH.

Procedure

All the experiments were done with Dowex 50 resin of mesh size 35-75 microns, as determined by sedimentation. The resin was in the ammonium form and had an exchange capacity of 5.2 milliequivalents per gram of dry resin.

Elution was carried out with 10^{-2} $\underline{M}$ EDTA, brought to the desired pH by neutralization with ammonia. The column had a cross-section of 0.78 cm^2; the weight of dry resin was of the order of 15 grams (free volume: about 10 ml.) Separations were carried out at ambient temperature.

A solution containing trace quantities of Ca^{45}, Sr^{90}, Ba^{140}, and Ra^{228} was loaded on the column at pH 3 and the tracers were eluted with EDTA, first at pH 7.4, then at pH 9, after the strontium. Fig. 13 shows the separation obtained.

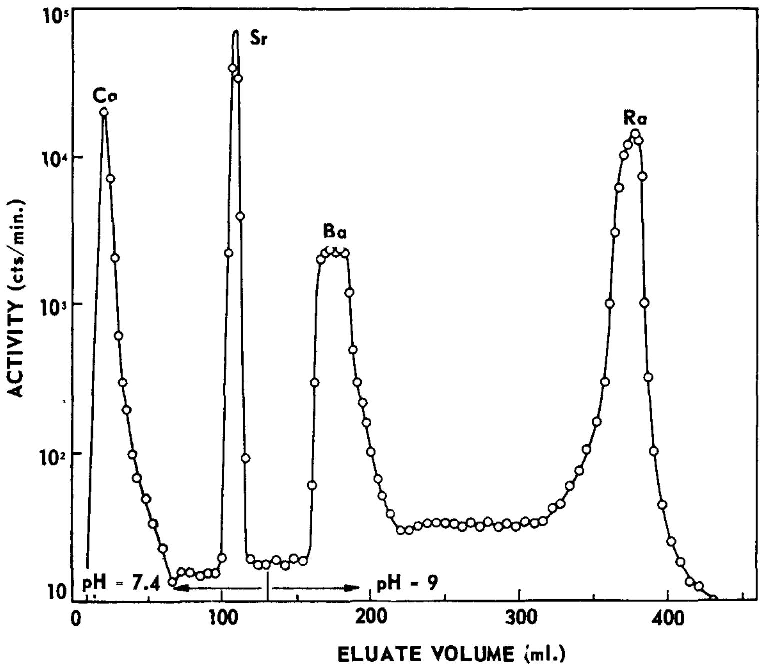


Fig. 13. Chromatographic separation of Ca, Sr, Ba, and Ra on Dowex-50 with EDTA.

Procedure 26

Preparation of Carrier-Free Radium-228[92]

Author's abstract

An ion-exchange process was developed for the production of carrier-free Ra^{228} and Ac^{228}. The Ra^{228} was produced from old $Th(NO_3)_4$. After a tributyl phosphate extraction of about 95% of the Th, the residuals were separated from the Ra^{228} on a Dowex 50x8 cation-exchange column in 0.5M NH_4-lactate solution. In the cation-exchange column, the Ra^{228} was bound. Rare earth impurities were removed from the column through elution by 0.7M

NH_4-lactate. The Ra^{228} was eluted by 3M HNO_3 and after the solution was concentrated by evaporation, it was transferred through 0.5 ml 0.05N HCl solution on a 0.3 x 8 cm cation-exchange column filled with Dowex 50x12 (400-mesh) resin. The Ac^{228} can be regularly eluted from the column by 0.65M NH_4-lactate, since under such conditions the adsorption zone of the Ra^{228} is shifting at a very low rate and the decomposition products Th^{228}, Pb^{212}, and Bi^{212} are eluted in precedence to the Ac^{228}. After acidification, the NH_4-lactate solution containing the Ac^{228} was carried over to a cation-exchange column from which first the Pb^{212} and Bi^{212} were eluted through 2N HCl, and then the Ac^{228} was eluted through 7N HCl. The radioactive contamination of Ac^{228} amounts to 0.2%, and its yield is 70 to 80% relative to the initial Ac^{228} content of $Th(NO_3)_4$.

Procedure 27

Determination of Traces of Actinium-227 in Purified Radium-223 [82]

(Note: This procedure was developed to evaluate the radiochemical purity of radium-223 used in a half-life determination.)

Principle

Actinium and thorium isotopes are separated from radium by coprecipitation on a rare earth phosphate at a controlled pH, in the presence of barium holdback carrier.

Procedure

To the sample to be analyzed for actinium and thorium, add two milligrams of lanthanum carrier and ten milligrams of barium carrier. Add one drop of methyl orange indicator, two drops of 85 per cent phosphoric acid, and distilled water to a volume of about ten milliliters. Begin stirring.

Add concentrated ammonium hydroxide dropwise until the color is definitely yellow. Add one normal nitric acid dropwise until the color is just pink. Add one drop of one normal ammonium hydroxide (yellow color) and add 0.1 normal nitric acid dropwise until the color is just pink. (Note - the color change is not sharp, and it is unwise to trust to memory with respect to the endpoint; hence, the repeated over-addition and back-titration of base and acid.)

Stir five minutes. Centrifuge five minutes, and discard the supernate (unless the radium-223 is to be recovered by precipitation of barium sulfate). To the precipitate add 10 milliliters of one normal nitric acid and begin stirring. Add 10 milligrams of barium carrier, one drop of 85 per cent phosphoric acid, and one drop of methyl orange indicator. Neutralize as before by the dropwise addition of concentrated ammonium hydroxide, one normal nitric acid, one normal ammounium hydroxide, and 0.1 normal nitric acid.

Stir five minutes. Centrifuge five minutes, and discard the supernate. Repeat the dissolution, additions, and precipitation as in the preceding paragraph.

Stir five minutes. Centrifuge five minutes, and discard the supernate. To the precipitate add 10 milliliters of 0.01 per cent dihydrogen ammonium phosphate solution. Stir vigorously five minutes. Centrifuge five minutes. Discard the supernate.

Mount the precipitate as a slurry in distilled water on a stainless steel disk previously prepared with a one-quarter inch retaining ring of collodion or Krylon plastic spray coating. Evaporate the slurry to dryness under an infrared lamp, and ignite the disk at red heat for 30 seconds. Allow six hours for the decay of lead-211, and alpha-count the sample periodically to determine the actinium-227 and thorium-227 by the method of differential decay.

The lanthanum phosphate precipitate was found to contain 0.001 per cent of the original radium-223, and approximately 90 per cent of the actinium and thorium isotopes.

Procedure 28

Isolation of RdTh (Th^{228}) from Radium-Mesothorium Preparations[60]

Principle

Radium is precipitated from mixtures of HBr, methyl alcohol, and ether.

Procedure

The Ra-MsTh preparation available to us contained 15.5 mg-eq of radium and radiothorium (determined in 1951). The starting product was dissolved in 0.15 ml methyl alcohol (0.1 N in HBr). $Ra(MsTh_1)Br_2$ was precipitated with 47% HBr (4:1 ratio between the volumes of the precipitant and the starting solution). The precipitate of Ra-$MsTh_1$ bromides was washed twice with 0.1 ml 47% HBr.

The $Ra(MsTh_1)Br_2$ precipitate was dried and redissolved in methyl alcohol. $Ra(MsTh_1)Br_2$ was precipitated again to ensure a more complete isolation of RaTh (and also of RaD and RaE). The results are given in Table VI.

We further separated RdTh from RaD and from Ra-$MsTh_1$ residues. The solution containing RdTh, RaD and traces of Ra was evaporated to dryness and the precipitate was then dissolved in methyl alcohol (0.1 N in HBr); a drop of $BaBr_2$ (~5 mg) was added to the solution, and the traces of Ra-$MsTh_1$ and RaD

Procedure 29

Separation of $MsTh_2$ (Ac^{228}) from $MsTh_1$ (Ra^{228})[94]

Principle

Radium-228 is coprecipitated as the bromide with carrier barium by the addition of ether to a methyl alcohol solution 0.1N in HBr.

Procedure

In our first experiments, the $MsTh_1$-$MsTh_2$ solution was prepared from an aged thorium salt by precipitating thorium hydroxide with CO_2-free ammonia. To retain $MsTh_1$ in solution, 20 mg $BaBr_2$ had been added before thorium was precipitated. The filtrate containing Ba and $MsTh_1$ was evaporated to dryness and calcinated in a platinum crucible to remove the ammonium salts. The residue was dissolved in a small amount of methyl alcohol (~2 ml) and acidified to 0.1 N with HBr. One and a half months after the solution had been prepared, the β-activity of 0.1 ml was 2730 ± 50 cpm (average for 3 samples). To 1 ml of this solution, we added 9 ml of saturated $BaBr_2$ solution in methyl alcohol (0.1 N in HBr). The resulting solution was used as the starting material in our experiments.

A sample of the starting solution (0.3 ml) was placed into a 2.5 ml test tube with a ground stopper. The precipitation of $Ba(MsTh_1)Br_2$ was carried out with ether, the volume of the were then precipitated with barium bromide by adding ether at a 5:1 volume ratio to the starting solution.

The RaD coprecipitated with $BaBr_2$ can be separated from the main bulk of barium by precipitating barium bromide with 47% HBr, as described above. RaD can be purified from RdTh and barium residues by precipitating RaD as sulfide. Along with RaD the lead which has built up in the radium-mesothorium preparation (RaG, ThD) is also isolated.

TABLE VI

Preparation	Content in the preparation (in mc)	
	of radium	of RdTh
Starting Ra-MsTh preparation	12.2 ± 0.6	1.4 ± 0.1
Centrifugate after 1st precipitation of Ra-$MsTh_1$	0.03 ± 0.01	1.3 ± 0.1
Ra($MsTh_1$)Br_2 precipitate	12.0 ± 0.6	0.1 ± 0.01
Centrifugate after 2nd precipitation of Ra-$MsTh_1$	0.02 ± 0.005	0.07 ± 0.001
Ra($MsTh_1$)Br_2 precipitate after 2nd precipitation	12.4 ± 0.6	~ 0.001

precipitant being five to six times the volume of the starting sample solution. The Ba($MsTh_1$)Br_2 precipitate was washed in 0.1 ml of 2:1 ether-ethanol mixture. The ether-alcohol solution of $MsTh_2$ was evaporated to dryness; the residue was dissolved in a small amount of dilute acid, then transferred onto a steel disc, evaporated again and, finally, its activity was measured using an end-window β-counter.

It was found that 78 to 89% of $MsTh_2$ is extracted into the ether-alcohol solution.

The results were used in the actual isolation of $MsTh_2$ from a radium-mesothorium preparation. For this purpose we used $Ra(MsTh)Br_2$, from which RdTh, ThB, RaD, RaE, Po, etc., had recently been removed. This preparation had not been used in actual work since 1945, and therefore its $MsTh_2$ content was assumed to be equal (in activity) to the RdTh content.

A small portion of the dry bromide was transferred into a micro test tube with a $BaBr_2$ solution in methyl alcohol (0.1 N̲ in HBr) containing 5 mg barium. $Ba(Ra, MsTh_1)Br_2$ was then precipitated with 5 volumes of ether. After centrifuging, samples were drawn from the ether-alcohol solution to determine its $MsTh_2$ and Ra content.

We further isolated $MsTh_2$ from all the available Ra-MsTh. Methyl alcohol (0.1 N̲ in HBr) was added to the initial $Ra(MsTh)Br_2$ until completely dissolved, and then $Ra(MsTh_1)Br_2$ was precipitated with 5 volumes of ether.

Our $MsTh_2$ preparation, however, had a half-life of 6.5 hrs, rather than 6.13; this was apparently due to small impurities of long-lived radioelements and their decay products.

We therefore attempted an additional purification of $MsTh_2$ by adding one drop of saturated $BaBr_2$ solution in methyl alcohol

(~10 mg $BaBr_2$) to the ether-alcohol solution and removing the precipitate.

The half-life of $MsTh_2$ was 6.2 to 6.3 hrs. The $MsTh_2$ yield after purification was 70 to 80%.

The isolation of $MsTh_2$ from the radium-mesothorium preparation, the purification from Ra-$MsTh_1$ traces and Pb isotopes included, takes 20 - 30 min. $MsTh_2$ can be isolated continuously for 1 to 1.5 months.

Procedure 30

Radium Determination by Means of Adsorption Plates[95]

Principle

Radium is adsorbed from solution on plates covered with a layer of gelatine mixed with a dispersion of barium sulfate.

Preparation of Adsorption Plates

One gram of ground photographic gelatine was allowed to expand in 6 ml of cold water and dissolved by heating at ca 70°C. Two ml 2M (NH_4) SO_4 was added in portions. The mixture was cooled to ca 45°C, and, over a period of about 20 seconds, 3 ml 1M $BaCl_2$ was added with stirring. This mixture was immediately poured over two glass plates (9 x 12 cm), which had been previously dipped in diluted water glass (1:100) and dried in a vertical position. After the gelatine had stiffened on the horizontally positioned plates, the plates were soaked for 15 minutes in 100 ml water containing from 0.5 to 1 ml formaldehyde (40% soln). After drying, the plates were cut into pieces of the proper size; necessary data can be written on the dried emulsion with pencil.

A properly prepared plate has particles of ca 1 micron in thickness, swells strongly in water, but does not become loose in 1M HCl after several hours. Coarse-grained plates can be used only for work with internal standards. Emulsions which are too hard are easily loosened from the glass and have a reduced adsorption capacity.

Procedure

The adsorption must be carried out by reciprocal movement of the plate and the solution. For routine work, it is most convenient to shake them in horizontally positioned reagent vessels in a continuously operating laboratory shaker with a speed of 3-4 cycles per second. Usually plates having an area of 8 cm^2 and 40 ml of solution are used. Thick-walled 60-ml reagent bottles are closed with rubber stoppers whose bottoms are covered with melted paraffin. Siliconed reaction bottles were used only for experiments with solutions having a pH above 3.3.

The adsorption is carried out in a "Universal buffer" consisting of 0.1 M primary sodium citrate, 0.1 M citric acid, 0.01 M complexone III + 0.2% dried egg albumin. In this medium, only lead isotopes in great excess interfere somewhat with the radium.

Procedure 31

Separation of Radium from Actinium and Francium on Paper Impregnated with Inorganic Ion Exchangers[96]

Procedure

Papers impregnated with zirconium phosphate (PZ) were prepared according to the technique described by Alberti and Grassini, (Procedure 41)[110]; papers impregnated with hydrated zirconium oxide (OZ) and zirconium tungstate (WZ) were prepared by similar methods: treatment of paper impregnated with zirconium oxychloride with ammonia or sodium tungstate.

The washed and dried papers are cut into strips (2 cm x 12 cm); all the chromatographies are descending and take place in an atmosphere of water vapor at 60°. The development of the chromatograms is made by passing a G-M counter in front of the paper strip; this sweep is carried out at regular intervals to identify the short-lived compounds.

Starting Material	Impregnation	Eluant and duration	R_f	
Ra^{228} and Ac^{228}	PZ	0.5 M NH_4Cl; 30 min.	Ra 0.85	Ac 0.1
Ra^{223} and Fr^{223}	OZ	0.1 M NH_4NO_3; 20 min.	Fr 0	Ra 0.85
Ra^{223} and Fr^{223}	WZ	0.1 M NH_4Cl; 20 min.	Ra 0	Fr 0.5

Procedure 32

Separation of Ra from Ac, Th, Pb, Bi, and Fr by Cation Exchange[97]

Principle

The Ac, Th and Ra are sorbed on the cation exchanger, while Pb, Bi, and Fr pass through with the HCl feed solution. Ra is selectively eluted with 3 M HNO_3.

Procedure

Each cation column consisted of 1.00 g (dry weight) of 200-400 mesh Dowex 50 (hydrogen form) contained in a glass tube 10 cm long and 6 mm in diameter sealed onto a reservoir 10 cm long and 3 cm in diameter. Both column and reservoir were jacketed at 60°. Before they were loaded, the columns were prepared by washing with water.

The actinium sample was dissolved in 5 ml of 2 M hydrochloric acid and the solution was warmed to 80° before it was fed to a cation exchange column without application of pressure. When the feed had passed, the column was eluted successively with hot 2 M hydrochloric acid, 3 M nitric acid and 6 M nitric acid; the first 5 ml of eluate was rejected and the remainder, which contained the radium and actinium, was collected in centrifuge tubes. The Th^{227} daughter of the actinium was left on the column.

The progress of this separation is illustrated in Fig. 14.

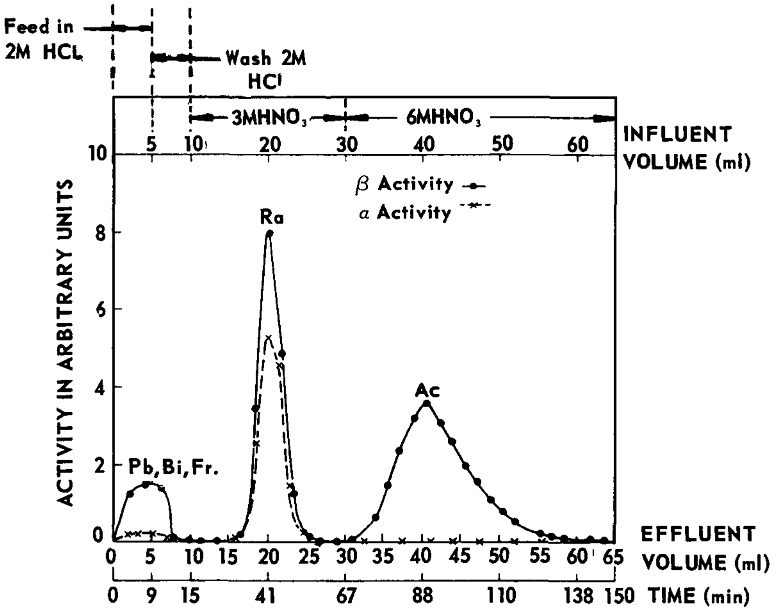


Fig. 14. The separation of Ac^{227} from its daughters by cation exchange chromatography.

(Reviewer's note: This procedure has numerous variations, and the reader is warned that the exact positions of the elution peaks should be determined separately for each batch of resin.)

Procedure 33

Separation of Radium and Barium by Cation Exchange[48]

Principle

Ba and Ra are sorbed on a cation resin column and eluted successively as citrate complexes.

Equipment and Reagents

Beds of 50- to 100-mesh Dowex 50 resin, 13 mm in diameter by 250 mm high, were prepared in borosilicate glass columns. The resin was washed with ethyl alcohol to remove soluble organic material. Conversion of the resin to the ammonium form and elimination of alkaline earths were accomplished by contact with excess 0.6M ammonium citrate, 1.5N in ammonium hydroxide.

Radium bromide was purchased from Eldorado Mining and Refining, Ltd. All chemicals used to prepare feed and eluting solutions were of reagent grade.

Experimental

Adsorption of Radium and Barium Feed solutions contained barium and radium salts dissolved in 0.2N nitric or hydrochloric acid. Flow rate of the feed solutions was limited to 1 ml per sq cm per minute to permit the cations to be adsorbed on the topmost layer of resin. Because anions were not adsorbed by the cation exchange resin, the nature of the feed solutions could be varied for convenience. If the starting form of the barium-radium mixture was a chromate precipitate (resulting from a concentration by fractional chromate precipitation), the barium and radium could be fed onto the eluting column and the chromate ion eliminated simultaneously. In this case the barium-radium chromate was dissolved in a small quantity of concentrated nitric acid and diluted to 0.2N acid concentration before feeding to the column.

Elution of Barium and Radium The elutriant addition rate was fixed at 0.3 ml per sq cm per minute. Most elutions were made at 25°C. Increasing the elution temperature to 50° and 75°C had an adverse effect on separation factors and increased the tendency for barium citrate to precipitate on the column. The column volume was taken as the volume of water (16.6 ml) required to fill the interstices of the air-dried ammonium resin form.

To check the effectiveness of barium elution by mineral acids and salts, a series of runs were made using 1 to 6<u>N</u> hydrochloric acid and 3.5<u>M</u> ammonium chloride solutions. Of all these elutriants tested, only ammonium chloride gave well defined barium peaks. The use of ammonium chloride as an elutriant did not provide a good separation of barium and radium, however. Better separations were obtained with citrate solutions at a pH above 5 than with ammonium chloride or citrate solutions of low pH. A typical separation is illustrated in Figure 15.

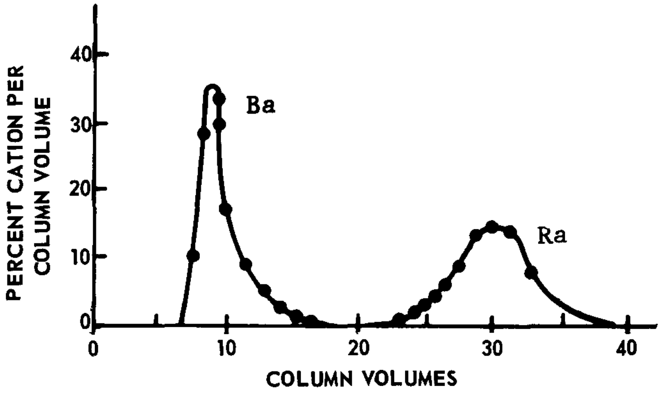


Fig. 15. Elution of barium and radium with 0.32M ammonium citrate at pH 5.6. (Barium, 120 mg. per sq. cm. Radium, 27 γ per sq. cm.)

Procedure 34

Separation of Ra from Pa, Ac, and Th by Residue Adsorption[101]

Principle

The mixture of trace radioelements is dried on a flat plate and leached with water. All but the Ra remain adsorbed.

Procedure

Evaporate a 1 N HNO_3 solution of actinium in equilibrium with its decay products on a platinum, gold, or stainless steel plate, keeping the temperature between 90° and 100°C. Cover the residue with distilled water and again evaporate to dryness.

Cover the residue with distilled water, heat two minutes at 90-100°C, and transfer the solution to another plate or to a vial. Repeat the leaching with fresh water.

Approximately 85% of the Ra^{223} is leached, with 12-15% of the actinium and 3% of the thorium. If protactinium is present, approximately 3% is transferred with the radium.

Further purification of the radium can be made by repeating the procedure starting with the leached solution.

Procedure 35

Extraction of Fr^{223} and Separation from Ra^{223} [42]

Principle

Ra and Fr are extracted by nitrobenzene, but the extraction of Ra is suppressed by the presence of EDTA.

Procedure

Fr^{223} and Ra^{223} were added as the chlorides to a pH9 buffer solution of sodium borate. The solution was made 0.05<u>M</u> in sodium tetraphenyl boron (previously purified by contact with $Al(OH)_3$ and filtered). Agitation for three minutes with an equal volume of nitrobenzene extracted more than 99% of the Fr and approximately 90% of the Ra.

If the aqueous phase is made 1% in EDTA (Na salt), the extraction of Ra is completely suppressed, while that of Fr is unaffected.

Fr and Ra can be recovered by washing the nitrobenzene with 1<u>N</u> HCl. One wash with an equal volume of aqueous solution removes the Ra completely; two washes are necessary for the Fr.

Procedure 36

Isolation of Actinium from Irradiated Radium[41]

Principle

Actinium and its decay products, except Ra and Fr, are chelated by thenoyltrifluoroacetone. Radium remains in the aqueous phase when the mixture is extracted with a benzene solution of TTA.

Procedure

If an aqueous solution of a mixture of ions in different oxidation states (Ac^{+3}, Ra^{+2}, Pb^{+2}, Bi^{+3}, Tl^{+3}, Th^{+4}, Po^{+4}) is brought into contact with a benzene solution of thenoyltrifluoroacetone, cations will be extracted into the benzene phase in a way which depends on the pH of the aqueous phase. In Fig. 16, the effect of variation of pH on the extraction of actinium, radium, and daughter elements into a benzene solution of thenoyltrifluoroacetone is shown, which illustrates the basis for the separation procedure. The higher the charge on the cation, the stronger the complex formed and the more acidic an aqueous solution from which it can be extracted. The solution of irradiated radium is adjusted to pH 2 with mineral acid and stirred with double its volume of 0.25M thenoyltrifluoroacetone (TTA) in benzene. After the phases separate, the benzene layer, which contains the thorium, polonium and bismuth is discarded. Fresh TTA solution is added and the acidity of the aqueous phase is adjusted to pH 5.5-6.0 by addition of base. After separation of the two immiscible phases, the aqueous phase is found to contain the radium, while the benzene phase contains the actinium and lead. By treating the benzene phase with water containing 0.1N acid, the actinium and lead are re-extracted into the water layer. The benzene layer is discarded. Lead is separated from the actinium by precipitation with carrier lead as lead sulphide, and the resulting supernatant solution, after filtration, is found to contain actinium free of daughter activities and radium. Milligram amounts of actinium have been prepared by this procedure.

(Reviewer's Note: The solution should be buffered with ammonium acetate; extraction with TTA tends to lower the pH of the aqueous phase.)

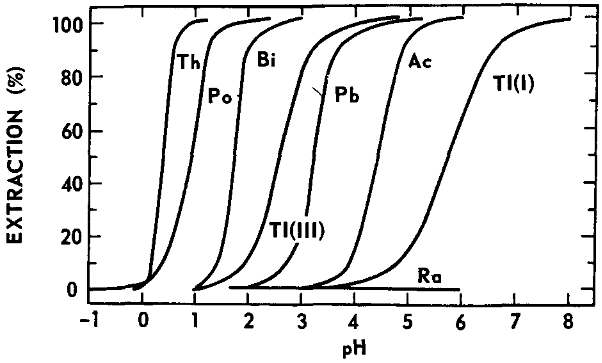


Fig. 16. Effect of pH on the extraction of actinium, radium, and daughter elements from aqueous solution by an equal volume of 0.25 M thenoyltrifluoroacetone in benzene.

Procedure 37

Purification of Radium by Dithizone Extraction[77]

Principle

Dithizone forms stable complexes with Pb, Bi, Po in chloroform over a pH range varying according to the element. Radium remains in the aqueous phase when its daughters are extracted as their dithizone complexes.

Procedure

A solution was prepared containing 3.2 millicuries of radium chloride in ca 7.5 ml of distilled water. The solution was brought to pH 9 with dilute NH_4OH and shaken vigorously for several minutes with an equal volume of dithizone in chloroform (ca 0.1 g/liter) The phases were allowed to separate, and the aqueous phase, containing the radium, was removed. At a pH in the vicinity of 9, the extraction yield is practically 100% for Pb, 70% for Bi, and 50% for Po. To be certain of eliminating all traces of Pb, four successive extractions were made. After this treatment, there remains, theoretically, about 8×10^{-3} of the RaE and 6×10^{-2} of the Po originally present.

The solution is then brought to pH 2 by the addition of dilute HCl, and the remaining RaE and Po are extracted with dithizone in chloroform. At a pH of approximately 2, the extraction yield for the Bi and the Po is of the order of 0.95. Four extractions were made to insure the complete absence of Po.

The radium remaining in the aqueous solution was found to be 3 millicuries.

Procedure 38

Separation of RaB (Pb^{214}) and RaC (Bi^{214}) from Ra^{226} [105]

Principle

Radium solutions are freed of all daughter products by anion exchange. The short-lived daughters are allowed to grow, and the emanation is driven out by bubbling. RaC and RaB are separated from Ra by cation exchange.

Procedure

A column of Nalcite WBR under 2N HCl is fed with a solution of 20 μC radium in 2 ml 2N HCl. After rejection of the first 3 ml of effluent solution, the column is washed with 6 ml 2 N HCl. The eluate is diluted with water to a concentration of 0.5 N HCl and set aside in a tightly stoppered flask to allow time for the growth of the short-lived decay products.

To drive the emanation out of the radium solution, we use wide-mouthed 50-ml Erlenmeyer flasks, two of which are connected in series like gas-washing flasks. The solution is in the first flask, and the second serves as a safety flask to collect any sprayed solution. A plug of glass wool is fitted loosely in the delivery tube for additional protection. A sintered glass filter stick serves as a gas delivery tube. The volume and flow rate of the inert gas must be so adjusted as to insure that all the emanation has been driven out of the solution.

A bubbling time of 7-10 minutes with a steady stream of CO_2 was found to be optimum for 30 ml of 0.5N HCl with a radium-equivalent of 20 μC. Shorter bubbling times do not completely drive out the emanation and the RaC solution is thereby significantly contaminated with RaB. Longer bubbling times result in a noticeable decrease in the activity due to the decay of RaC in the emanation-free solution.

According to the desired amount of RaC, an aliquot of the emanation-free radium solution is passed through a cation exchange column in 0.5 N HCl, followed by a wash of 10 ml of 0.5 N HCl. We use the strongly acidic Nalcite HCR, which is converted to the hydrogen form with 6N HCl and stored under 0.5 N HCl.

The yield of the eluted RaC decreases with decreasing HCl concentration. Quantitative elution of RaB is possible with 2N HCl.

The radium-loaded cation exchange column cannot be used as a generator for RaC or RaB, because the long-lived emanation diffuses quite rapidly through the column, so that, within a short time, most of the short-lived decay products are dispersed through the interstitial solution.

Procedure 39

Separation of Radium and its Long-Lived Decay Products by Paper Electrochromatography[106]

Principle

The cations are separated in an electric field by their different rates of migration through moist paper.

Materials and Apparatus

The moistened paper wrapped in polyethylene sheeting (0.005 inch thick) was supported on a Thermopane window (nearly 1 or 2 meters long) cooled with running water.

The electrode vessels were made of plastic (Lucite). They were provided with electrodes of large, flat strips of graphite supported edgewise in the solution and separated from the paper by an upright sheet of plastic extending nearly to the bottom of the vessel. The direct current potential was obtained from an electronic rectifier that provided about 800 volts.

The paper employed in these experiments was Eaton-Dikeman grade 301, 0.03 inch thick. This wood-pulp paper was employed without treatment and also after thorough extraction by downward percolation with (1$\underline{M}$) nitric acid, (1$\underline{M}$) acetic acid, and water. The unwashed paper contained about 0.12% ash which was some 46% calcium. The washed and dried paper contained about 0.01% ash which was about 0.9% calcium. The paper strips were several centimeters longer than 1 or 2 meters and were arranged so that there were either 1 or 2 meters of paper between the solutions in the electrode vessels.

Procedure

Before use, the paper was moistened with the electrolytic solution, usually 0.1M lactic acid. It was blotted lightly and wrapped in the polyethylene sheet, and the ends were placed in the electrolytic solution (about 8 liters in each electrode vessel). With the polyethylene wrapping opened momentarily, the solutions to be examined (about 50 µL each) were added at marked starting points, and the migration was carried out for some 20 to 24 hours with 3.5 or 7 volts per cm. After the migration, the zones containing nonradioactive ions were located by spraying the paper with solutions of sodium sulfide or hydrogen sulfide for lead and bismuth and with sodium rhodizonate for barium. The paper was then dried, and the zones of radioactive ions were located by autographic methods using several juxtaposed sheets of Kodak No-screen x-ray film 14 X 17 inches (exposure about 8 to 16 hours).

Small scale separations of radium from its daughters were performed rapidly in hardened filter paper moistened with 0.1M lactic acid. With as little as 1 µL of solution containing only 0.05 γ of radium, the separation of radium, lead, bismuth, and polonium was completed quantitatively in less than 1 hour.

Procedure 40

Recovery of Radium Isotopes from Thorium and Lead Targets[107]

Principle

Coprecipitation of radium with barium chloride from cold HCl leaves thorium or lead in solution.

Procedure

Thorium targets were dissolved in HCl (with ammonium fluosilicate catalyst added), the solutions were saturated with HCl gas and cooled in ice. The $BaCl_2$ precipitate was brought down within five to ten minutes after the end of bombardment. The precipitation was made from about 10 ml of HCl using about 1 mg of barium carrier. Because of the presence of large amounts of higher mass radium isotopes and their daughters, it was not possible to subject such samples to alpha-spectrum analysis directly to obtain information on neutron-deficient radium isotopes. The emanation daughters of such activities could be studied by dissolving the $BaCl_2$, and later sweeping the emanation daughter activity from the solution.

A fast method was also developed for removing radium from lead targets bombarded with carbon ions in the 60-inch cyclotron. The lead was dissolved in a minimum amount of hot 2 to 3 $\underline{M}$ HNO_3, and the solution was saturated with HCl gas and cooled in ice. In saturated HCl the lead forms a soluble chloride complex. Barium carrier (a few tenths of a milligram) was then added to precipitate $BaCl_2$ to carry the radium. With sufficient barium carrier and time to complete the precipitation, one would expect quantitative yields. The precipitation is not instantaneous, however, and $BaCl_2$ is slightly soluble even in saturated HCl. To obtain thin samples for pulse analysis in a short time, incomplete precipitation of the barium chloride was tolerated, and yields were sometimes as low as 20 per cent, judging from tracer runs with Ra^{226}. Samples could be prepared in five to ten minutes.

Procedure 41

Chromatography on Paper Impregnated with Zirconium Phosphate[110]

Principle

Filter paper impregnated with zirconium phosphate (ZP) has the same elution characteristics as inorganic ion exchange columns, permitting separation of radium from alkaline earths and other metal ions.

Preparation of the ion-exchange paper

Strips (6 x 40 cm) of Whatman No. 1 filter paper were drawn as uniformly as possible through a 30% solution of $ZrOCl_2$ in 4 $\underline{N}$ HCl. After this impregnation the strips were quickly placed, for 5 min, on pieces of filter paper, which immediately absorb the excess liquid. The impregnated paper was then dried at room temperature by placing it on another sheet of filter paper. The dry strips were then dipped for 2 min into a 60% solution of H_3PO_4 in 4 $\underline{N}$ HCl, and dried at room temperature. After 6 h the excess H_3PO_4 was removed from the strips by washing them first in 2 N HCl for 10 min and then twice in H_2O.

In order to increase the ZP exchange capacity, an additional treatment with the same 60% solution of H_3PO_4 in 4 N HCl was carried out and afterwards the strips were put into an oven at 50° for 75 min.

As described above, the strips were subsequently washed with 2 N HCl, H_2O and left to dry in the air.

It is important to note that special chromatographic paper is not required for the preparation of these strips. Ordinary filter paper can be used because the R_F value depends essentially on the type of ion exchange employed. In any case all that is required to obtain the same results is to employ the same type of paper and above all to standardize the preparation of the sheets as far as possible, so that the same quantity of ions per unit area is obtained.

Experimental

The solutions of metal ions were prepared by dissolving the chlorides.

The chromatogram (Whatman No. 1 filter paper impregnated with $3.5\ mg/cm^2$ of ZP) was 40 cm long and the starting point was situated at 3.5 cm from one end. The strip was developed by the ascending method, with HCl of various concentrations, for 4 - 8 hours. In Table VII the R_F values obtained are given. The values reported show that it is possible to carry out several separations by employing this eluent.

On studying the behaviour of alkaline earths and alkali metals it was found that the same order of adsorption is obtained on ZP-impregnated paper as on ZP columns.

Table VII

R_F VALUES IN 0.1 N HCl

Element*	R_F
Hg(II)	0.67
Cd(II)	0.60
Cu(II)	0.59
Fe(III)	0
Al(III)	0.13
**Cr(III)	0.75
Mn(II)	0.60
Ce(III)	0.19
La(III)	0.31
Ti(IV)	0
UO_2(VI)	0
Th(IV)	0
Co(II)	0.67
Ni(II)	0.61
**Zn(II)	0.69
**Ca(II)	0.81
**Sr(II)	0.81
Ba(II)	0.60
***Ra(II)	0.44
Mg(II)	0.76
Li(I)	0.82
Na(I)	0.68
K(I)	0.53
Rb(I)	0.12
**Cs(I)	0

*The spots were detected by spraying the strips with suitable reagents.

**Starred elements were also detected by radiochemical methods.

***Only radiochemical methods were employed for radium.

Procedure 42

Separation of Ra from Ac, Th, Pb, and Bi by High Voltage Paper Electrophoresis[111]

Principle

Application of a high voltage gradient accelerates the migration of ions and permits separation of species having similar rates of mobility.

Procedure

The apparatus we developed is based on that described by Gross[112]. The heat released during the electrophoresis is dissipated by the circulation of water or of a refrigerant liquid in two aluminum plates pressed uniformly against the paper. The plates are electrically insulated by thin sheets of polyvinyl chloride between which the electrophoretic band is slipped. The temperature of the paper, on the average, is 15°C. The high voltage is supplied by a constant high voltage generator having a range of 0-5 kV and a maximum current intensity of 500 mA. The dimensions of the paper strips (Arches No. 302) are 44 x 3 cm. The positions of the radioelements, after electrophoresis, are determined by moving the paper strip under an appropriate detector (alpha or beta scintillation counter) and the separated isotopes are identified by their radiation or their half-lives. In the case of short-lived radioelements (30 minutes or less) or of weak activity, the paper is cut into one centimeter sections. The movement of the activity from the various samples is determined with the aid of a very sensitive counter or of a low background counting system, allowing histograms of the activity of the band to be traced at a given instant.

The results for the electrophoresis of Ac^{227} and Ra^{228} in various complexing media are given in Table VIII. In all cases, the electrolyte concentration was 0.05 $\underline{M}$, the voltage was 500 volts, the duration 35 minutes, and the temperature 15°C. The complexing media were the ammonium salts of citric acid (CIT), nitrilotriacetic acid (NIT) and ethylenediamine tetraacetic acid (EDTA).

Table VIII

SEPARATION OF Ac^{227} AND Ra^{228} FROM THEIR DESCENDANTS BY HIGH-VOLTAGE ELECTROPHORESIS

Starting Material	Migration Towards Anode (Centimeters)				
	Th	Ra	Pb	Ac	Bi
Ac^{227} (NTA)	0	10.5	18.4	26.4	-
Ac^{227} (EDTA)	0	23.4	27.8	15.3	-
Ac^{227} (CIT)	31	9	24	28	-
Ra^{228} (NTA)	0	5.7	20	26.4	31.2
Ra^{228} (EDTA)	0	19.2	25.2	11.2	13
Ra^{228} (CIT)	33.4	9	26.8	30.8	32.1

Procedure 43

Determination of Radium-226 in Mill Effluents[114]

Principle

Radium is coprecipitated with lead and barium sulfates, and the precipitate is redissolved in alkaline EDTA. Barium-radium sulfate is reprecipitated at pH 4-5, and radium-226 is determined by alpha-counting and differential decay analysis.

Sample Preparation

There has been some disagreement as to whether or not aqueous samples should be acidified before taking an aliquot for analysis and thereby to include some radium that may have been insoluble at the time of sampling. It is the feeling of the present authors that any radium that can be dissolved in dilute acid should be included in the analysis. Otherwise, radium that is insoluble at the point of sampling due to local conditions such as adsorption on hydrolytic precipitates, silt or walls of the container could be redissolved on further dilution or other changing conditions. Soluble radium would then be available at the point of intake for incorporation into the human food chain at concentrations higher than the analyses would indicate. On the other hand, severe treatment is not desirable, since radium present in highly insoluble materials such as grains of sand and other naturally insoluble materials is not likely to constitute a significant hazard.

Add sufficient concentrated nitric acid to make the sample 2% acid by volume and mix thoroughly. Let the solution stand for at least 30 minutes, again shake vigorously and immediately withdraw an aliquot for analysis into a graduated cylinder. A representative quantity of any finely-divided insoluble material should be included if the total quantity is small. If large quantities of river sediment are present, let the sample stand over night after acidification and thorough mixing. Remove an aliquot without disturbing the solid material in the bottom of the container.

Determination of Radium

Transfer 1500 ml of the acidified sample to a clean 2-liter beaker and add 4 to 6 drops of 0.1% m-cresol purple indicator and 4 drops of 1% aerosol solution. Adjust the pH to 1 to 2 by adding ammonium hydroxide until the indicator just changes to yellow and then add nitric acid until the color just turns red. Add 5 mg of barium and 200 mg of lead carriers while stirring the solution vigorously. Continue stirring and add 50 ml of 50% ammonium sulfate solution to precipitate lead and barium sulfates. Allow the precipitate to settle and decant as much of the supernate as convenient without disturbing the precipitate. Filter the remaining solution through quantitative filter paper using paper pulp to insure complete retention of the precipitate. Discard the filtrate.

Place the filter paper containing the lead and barium sulfates in a 250-ml Erlenmeyer flask and add 15 ml of concentrated nitric acid and 7 ml of 72% perchloric acid. Destroy the filter paper by heating to fumes of perchloric acid. If the sample becomes dark-colored just prior to the evolution of fumes, add a few drops of nitric acid to the hot solution to oxidize the remaining organic material. The lead and barium sulfates will go into solution in the fuming perchloric acid, thus insuring complete solution of all radium present except that which may be in the insoluble silica carried from the sample with the lead and barium sulfates. Evaporate the perchloric acid solution to incipient dryness and cool. Lead and barium sulfates will reprecipitate from the solution. Add 5 ml of water, 10 ml of 10% EDTA-1.5% TEA (triethanolamine) solution, and 2 drops of m-cresol purple indicator. Add 4 $\underline{N}$ sodium hydroxide until the indicator just turns purple and then 10 drops excess. Place the flask on the hot plate and boil the solution for five minutes to insure solution of lead, barium, radium, radium daughters, and any thorium present, as EDTA or TEA complexes.

Cool the sample and filter through quantitative filter paper using paper pulp into a 40-ml centrifuge tube to remove any material insoluble in alkaline EDTA-TEA solution. At high pH in the absence of TEA thorium hydroxide will precipitate slowly from an EDTA solution and will not redissolve when the pH is subsequently lowered to precipitate the barium sulfate. TEA holds the thorium in solution even at high pH, while EDTA is effective at lower pH values, including the pH of the barium sulfate precipitation.

Wash the filter paper with an alkaline 1% EDTA-0.15% TEA solution, catching the washings in the centrifuge tube. Discard the filter paper. Add one milliliter of 20% sodium sulfate and 2 drops of methyl purple indicator (available from Fleischer Chemical Co.) to the solution in the centrifuge tube. Adjust the pH to approximately 4 to 5 by dropwise addition of glacial acetic acid until the methyl purple indicator just turns from green to purple, and then add approximately one milliliter excess. Barium and radium sulfates will precipitate at this pH from the EDTA-TEA solution, leaving lead, radium daughters, and any thorium present in solution. Centrifuge to collect the precipitate and discard the supernate. Slurry the precipitate with 5 ml of water and 5 ml of 10% EDTA-1.5% TEA solution. Add 2 drops of m-cresol purple indicator and repeat the pH adjustment with 4 N sodium hydroxide as described above. Heat in a boiling water bath for five minutes to redissolve the barium sulfate. Cool, add one milliliter of 20% sodium sulfate and repeat the barium sulfate precipitation with glacial acetic acid as before. Centrifuge, discard the supernate, and slurry the precipitate with 10 ml of distilled water. Centrifuge and discard the wash water. Slurry the precipitate with 1 to 2 ml of distilled water and transfer quantitatively to a 2-inch serrated stainless steel planchet. Dry the sample under an infrared lamp. muffle at 500°C. for 10 minutes, cool, and α-count in a gas-flow proportional counter for 30 minutes at 3 hours following the second barium sulfate precipitation.

Three hours after the barium sulfate separation, the alpha activity counted will include all radium isotopes present and their respective daughters which have grown in during this period. In particular, the alpha activities from uranium mill effluents will result from radium-226 and radium-223 and its daughters; radon-219, polonium-215, and polonium-211.

In order to determine the radium-226 activity, a second alpha count must be made at a designated interval following the barium sulfate precipitation such that sufficient growth of the radium-226 daughters and simultaneous decay of radium-223 and its daughters will enable one to calculate the actual radium-226 activity. For example, the activity of the sample may be determined at 3 hours and one week after the barium sulfate precipitation and the radium-226 calculated from the two counts as follows:

$$(1) \quad A_2 = X + 3X(1 - e^{-\lambda_1 t_2}) + 4Y\, e^{-\lambda_2 t_2}$$

$$(2) \quad A_1 = X + 3X(1 - e^{-\lambda_1 t_1}) + 4Y\, e^{-\lambda_2 t_1}$$

A_1 and A_2 are the total activities at times t_1 and t_2, respectively; X is the radium-226 activity, Y is the radium-223 activity, λ_1 is the decay constant of radon-222 controlling the rate of growth of radium-226 daughters, and λ_2 is the decay constant of radium-223, which controls the decay of the radium-223 chain after approximately the first three hours. (Lead-211 builds up in the radium-223 chain with a half-life of approximately 36 minutes, controlling the growth of its alpha-emitting daughters, bismuth-211 and polonium-211. After three hours, only a very minor error is introduced if this growth is neglected in determining the decay of the radium-223 chain.) Now if the exponentials in equations (1) and (2) are evaluated for counting times t_1 equals 3 hours and t_2 equals 1 week, and equation (2) subtracted from equation (1) in order to eliminate the Y term, it is found that

$$(3) \qquad X = \frac{A_2 - 0.66\ A_1}{2.46}\ .$$

Thus the radium-226 activity can be found from the two counts provided that radium-226, radium-223, and their daughters are the only alpha emitters present on the counting plate.

After the radium-226 activity has been determined as above, the concentration of radium-226 in microcuries per milliliter of sample may be calculated by multiplying the counts per minute by 7.9×10^{-10}. This factor is obtained as follows:

$$\frac{1\ \text{c/m}}{\text{counting efficiency} \times \text{d/m/}\mu\text{c} \times \text{sample volume} \times \text{chem yield}}$$

Counting efficiency is 0.40, d/m/μc is 2.22×10^6, sample volume is 1500 ml, and chemical yield as determined from samples spiked with known radium-226 is 95%.

Excellent decontamination of radium from daughter products and thorium isotopes is obtained with the described procedure. The decontamination factor is greater than 10^5 for thorium and greater than 2×10^4 for polonium.

(Reviewer's note - The authors state that error due to radium-224 is not eliminated by this method, but none has been encountered in any of their samples. Radium-224 would, however, be expected in effluents from sources rich in thorium-232. In such cases, the differential decay analysis of Procedure 15, page 147, could be applied if the final EDTA solution were divided in half and the barium-radium sulfate reprecipitated and mounted on two different days.)

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