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The Radiochemistry of Rubidium

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The Radiochemistry of Rubidium

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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 nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of rubidium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of rubidium which might be included in a revised version of the monograph.

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The Radiochemistry of Rubidium

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I. GENERAL REFERENCES ON THE INORGANIC AND ANALYTICAL CHEMISTRY OF RUBIDIUM

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II. RADIOACTIVE NUCLIDES OF RUBIDIUM

The radioactive nuclides of rubidium that are of interest in the radiochemistry of rubidium are given in Table I. This table has been compiled from information appearing in reports by Strominger, et al.,(1) and by Hughes and Harvey.(2)

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*Operated for U. S. Atomic Energy Commission by Union Carbide Corporation.

III. THE CHEMISTRY OF RUBIDIUM AND ITS APPLICATION TO THE RADIOCHEMISTRY OF THE RUBIDIUM RADIONUCLIDES

Radiochemistry is probably best described as being an analysis technique used primarily either (1) to assist in obtaining a pure radionuclide in some form so that an absolute measurement of its radioactivity, radiation energies and half-life can be made, or (2) to determine the amount of a particular radioelement in a radionuclide mixture, or (3) to complete a radioactivation analysis being used to determine the concentration of a specific stable element in a particular sample material. In order to be an aid in accomplishing any one of the above interests, radiochemistry usually considers the isolation of the desired radionuclide by either <u>carrier</u> or <u>carrier-free</u> separation methods.

Generally, <u>carrier</u> methods are used most frequently in radiochemistry. They involve the addition of a small amount of inactive stable element to a solution of the irradiated material to serve as a carrier of the radionuclide of that element through the separation method. In <u>carrier-free</u> separations, i.e., radiochemical techniques used mostly for absolute radioactivity measurements, it is required that the radioelement be isolated in a manner capable of giving either no amount or a minimal amount of stable element in the final form to be used in the radioactive measurements.

In most instances, analytical radiochemistry is dependent upon more conventional ideas in analytical chemistry involving separations by such methods as precipitation, solvent extraction, chromatography, volatilization, and/or electrolysis and the subsequent presentation of the isolated radioelement in a form suitable for a measurement of the radioelement's radioactivity. One major difference exists between <u>carrier</u> radiochemistry and more conventional techniques in that it is not always necessary to recover completely the added amount of <u>carrier</u> element, since a radiochemical analysis is designed to assure that the atoms of a radioactive element achieve an isotopic state with the atoms of the inactive element, and any loss of the radioactive species is proportional to the "loss" of carrier during the separation process.

Colorimetric, polarographic, and similar analysis techniques are seldom used in radiochemistry, because they do not separate the desired radionuclide from contaminants (either radioactive or stable) in the mixture being analyzed. However, some of the developments used in these analysis techniques may be useful in radiochemistry.

TABLE I

THE RADIOACTIVE NUCLIDES OF RUBIDIUM

Radionuclide	Half-life	Mode of Decay	Energy of Radiation, Mev	Produced by
Rb^{81}	4.7 h	EC, β^+	β^+: 0.99 γ: 0.95 abs	Br-α-2n
Rb^{82m}	1.25 m	β^+		Daughter Sr^{82}
Rb^{82}	6.3 h	EC, β^+	β^+: 0.775, 0.175 γ: 0.188, 0.248, 0.322, 0.390, 0.690, 1.314, 0.423, 0.465, 0.558, 0.610, 0.768, 0.818, 1.02, 1.464	Br-α-n, Kr-d-2n
Rb^{83}	83 d	EC	γ: 0.45, 0.15	Br-α-2n
Rb^{84m}	23 m	IT, EC	γ: 0.463, 0.239, 0.890	Br-α-n, Rb-n-2n
Rb^{84}	34 d	EC, β^+, β^-	β^+: 1.629, 0.822, 0.373 γ: 0.890	Br-α-n, Kr-α-pn, Rb-n-2n, Sr-d-α
Rb^{85m}	0.9 x 10^{-6} sec.	IT	γ: 0.513	Daughter Sr^{85}
Rb^{86m}	0.99 m	IT, EC	γ: 0.57, 0.78	Rb-n-γ, Rb-n-2n
Rb^{86}	19.5 d	β^-	β^-: 1.82, 0.72 γ: 1.076	Rb-n-γ, Rb-γ-n, Sr-d-α, Fission U
Rb^{87}	6.0 x 10^{10} y	β^-	β^-: 0.275	Fission U Parent Sr^{87}
Rb^{88}	17.8 m	β^-	β^-: 5.3, 3.6, 2.5 γ: 2.8, 1.86, 0.90	Rb-n-γ Fission Th-U-Pa Daughter Kr^{88}
Rb^{89}	15.4 m	β^-	β^-: 4.5 abs	Fission U
Rb^{90}	2.74 m	β^-	β^-: 5.7 abs	Fission U
Rb^{91}	1.67 m	β^-	β^-: 4.6 abs	Fission U
Rb^{91}	14 m	β^-	β^-: 3.0 abs	Fission U
Rb^{92}	80 s	β^-		Fission U
Rb^{93}	Short	β^-		Fission U
Rb^{94}	Short	β^-		Fission U
Rb^{95}	Short	β^-		Fission U
Rb^{97}	Short	β^-		Fission U

The information that follows generally describes the chemical behavior of rubidium and its compounds. Many of these reactions have been used or can be used in devising radiochemical analysis methods for the rubidium radionuclides. More detailed information on the inorganic and analytical chemistry of rubidium can be obtained either from the references cited in this section or from the general references given in Section I of this monograph.

A. The General Chemistry of Rubidium

Rubidium occurs only in minute amounts accompanying the other alkali metals.(3) Lepidolite ores can contain as much as 1% rubidium; carnallite contains about 0.015%.

Metallic rubidium is best prepared by chemical methods involving either the heating of its hydroxide with metallic magnesium in a current of hydrogen or with metallic calcium in a vacuum.(4) Small amounts of rubidium metal can also be formed by heating the chloride compounds, mixed with barium azide, in a vacuum.

1. Metallic Rubidium

Rubidium metal is a soft, silver-white metal having a density of 1.52. It will melt at 39° C and has a boiling point of 696° C.

Rubidium will tarnish in air, and it will react vigorously with water. It is easily dissolved in liquid ammonia. Rubidium amide, $RbNH_2$, can be formed if ammonia gas is passed over molten rubidium metal. Rubidium also reacts directly with nitrogen, and it will ignite upon exposure to oxygen.

2. The Chemical Compounds of Rubidium

Rubidium, like all the other alkali metals, has only a +1 oxidation state. Its chemical properties are similar to those of the other alkali metals. It will react with carbon dioxide, hydrogen, oxygen, nitrogen, sulfur, and the halogens. The reactions of rubidium with these and other elements is presented in some detail below. Table II shows the solubility of many of the rubidium compounds in water and other reagents.

Table II. Solubility of Rubidium Compounds

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Bromides	$RbBr$	98^{5}	$205.2^{113.5}$	Slightly soluble in acetone; insoluble in alcohol
	$RbBrO_3$	2.93^{25}	5.08^{40}	
	$RbBr_3$			
Chloride	$RbCl$	77^{0} 91.2^{20}	138.9^{100}	0.08^{25} alcohol; very slightly soluble in NH_3; insoluble in alcohol
	$RbClO_3$	5^{19}	62.8^{100}	
	$RbClO_4$	0.5^{0}	18^{100}	Insoluble in alcohol
Fluorides	RbF	130.6^{18}		Soluble in dilute HF; insoluble in alcohol, ether and NH_3
Iodides	$RbIO_3$	2.1^{25}		Very soluble in HCl
	$RbIO_4$	0.65^{13}		
	RbI	152^{17}	Very soluble	0.674^{25} acetone
	RbI_3	Soluble		
Nitrates	$RbNO_3$	3.48^{20}	452^{100}	Very soluble HNO_3; soluble in acetone
Oxides	Rb_2O	Soluble; Decomposes	Soluble; Decomposes	
	Rb_2O_2	Decomposes to $RbOH + H_2O_2$		
	Rb_2O_3	Soluble; Decomposes		
	RbO_2	Decomposes to $RbOH + H_2O_2 + O_2$		
Carbonates	Rb_2CO_3	Very soluble	Very soluble	
Sulfides	Rb_2S	Very soluble	Very soluble	
	Rb_2S_2			
	Rb_2S_3			
	Rb_2S_5	Decomposes	Decomposes	Soluble 70% alcohol; insoluble in ether and chloroform
	Rb_2S_6			
Sulfates	Rb_2SO_4	Very soluble	Very soluble	
Phosphates	Rb_3PO_4, etc.	Very soluble	Very soluble	

a. Rubidium Hydride, RbH. Rubidium combines directly with hydrogen on heating to form RbH. It is less stable than LiH, and its colorless crystals decompose rapidly on heating and vigorously reacts with water to produce hydrogen gas.

b. The Oxides of Rubidium. Rubidium oxide, Rb_2O, can be produced by heating rubidium nitrite with rubidium azide, in the absence of air. If rubidium metal is burned in oxygen, rubidium dioxide, RbO_2, will be formed. RbO_2 is readily fusible, and it can give up its oxygen to an oxidizable substance when heated.

c. Rubidium Hydroxide, RbOH. Rubidium hydroxide can be prepared either by the electrolysis of aqueous rubidium chloride, RbCl, solutions or by reacting Rb_2SO_4 with barium hydroxide. RbOH is highly deliquescent, and it is very soluble in water and alcohol. Its chemical behavior is similar to that of potassium hydroxide, KOH. It forms strong basic solutions, and it can be readily volatilized when strongly heated.

d. *The Nitrogen Compounds*. Rubidium can react with nitrogen in an electric discharge tube to form either *rubidium nitride*, Rb_3N, or *rubidium azide*, RbN_3. These salts are highly colored, and they can be rapidly decomposed by water or alcohol to produce RbOH and NH_3.

Rubidium nitrate, $RbNO_3$, is isomorphous with potassium nitrate, KNO_3. It is more soluble in hot water than in cold, and it will form addition compounds with HNO_3 that have similar compositions and behavior as those formed by KNO_3 in its reactions with nitric acid.

e. *The Sulfide and Sulfate Compounds*. Rubidium will react with sulfur in varying amounts to form a series of sulfide compounds, e.g., Rb_2S, Rb_2S_2, Rb_2S_3, Rb_2S_5, Rb_2S_6. Most of the sulfide compounds are soluble, or will decompose in water or alcohol.

Rubidium sulfate, Rb_2SO_4, is isomorphous with potassium sulfate, K_2SO_4. Its melting point is at 1074° C, and it will form mixed salts with sulfates of aluminum, iron, and the bivalent metals. Most of the sulfate compounds are soluble in water. *Rubidium bisulfate*, $RbHSO_4$, can be produced by heating a mixture of Rb_2SO_4 and H_2SO_4. $RbHSO_4$ will dissolve in water to give an acidic solution.

f. *The Halogen Compounds of Rubidium*. *Rubidium fluoride*, RbF, can be obtained by neutralizing hydrofluoric acid with RbOH. *Rubidium chloride*, RbCl, can be obtained by a neutralization of the carbonates or by an ignition of the chloroplatinates. If a hot solution is treated with bromine or iodine, *rubidium bromide*, RbBr, and *rubidium iodide*, Rb, can be produced. All of the rubidium halide salts are completely ionized and are readily soluble in water at room temperature.

Rubidium chlorate, $RbClO_3$, or *rubidium perchlorate*, $RbClO_4$, are salts of the oxygen acids of the halogens. They can be prepared in the same manner as the potassium salts.

g. *The Phosphate Compounds of Rubidium.* Rubidium hydroxide, like potassium hydroxide, can also enter into reaction with H_3PO_4 to form various phosphate compounds, chief of which is Rb_3PO_4. The phosphate compounds are very soluble in water, and their aqueous solutions vary in their acidity and alkalinity. Rb_3PO_4 is stable toward heat.

h. The Carbonate Compounds. Rubidium carbonate, Rb_2CO_3, is prepared by treating Rb_2SO_4 with barium hydroxide and evaporating with ammonium carbonate. Rubidium hydrogen carbonate, $RbHCO_3$, is produced either by passing carbon dioxide gas into a saturated solution of Rb_2CO_3 or by passing carbon dioxide over a mixture of Rb_2SO_4 and charcoal. Rb_2CO_3 and $RbHCO_3$ solutions are alkaline because of the basic action of CO_3^{--} ions and the slight hydrolysis of the HCO_3^- ions.

i. Other Rubidium Compounds. Permanganate, $RbMnO_4$; chromate, Rb_2CrO_4; dichromate, $Rb_2Cr_2O_7$; hexachloroplatinate, Rb_2PtCl_6; alum, $RbAl(SO_4)_2 \cdot 12H_2O$; and hydrogen tartrate, $RbH(C_4H_4O_6)$, compounds of rubidium are known. All of these compounds are formed from similar chemical reactions used to form the corresponding potassium salts. Their reactions with other chemical agents are very similar to those for the potassium salts.

B. The Analytical Chemistry of Rubidium

Rubidium can be determined gravimetrically as RbCl, $RbClO_4$, Rb_2SO_4, or $Rb_2(PtCl_6)$.(5) An alcoholic solution of tin chloride has also been mixed with a concentrated HCl solution of RbCl to produce the hexachlorostannate compound, $Rb_2(SnCl_6)$.(6) Dipicrylamine has also been used to produce the compound , $(NO_2)_3C_6H_2{:}NRb \cdot C_6H_2(NO_2)_3$. 6-chloro-5-nitro-m-toluene sulfonic acid will produce the sulfonate compound, $CH_3 \cdot C_6H_2(Cl)(NO_2)SO_3Rb$.(7)

Duval,(5) in his pyrolysis studies, has shown that these compounds are suitable for the gravimetric determination of rubidium. Thus, these compounds can also be used in the radiochemical analysis of sample materials for the radioactive rubidium isotopes.

The isolation and separation of rubidium from other elements has been completed by such analytical techniques as precipitation, solvent extraction, and chromatography. These separation methods can generally be described as follows:

1. Separations By Precipitation. Rubidium and the other alkali elements (sodium, lithium, potassium, and cesium) can be best separated from other elements by the methods of Berzelius(8) and Smith.(9) The

Berzelius method(8) and its modifications(10-12) uses mixtures of HF-$HClO_4$-H_2SO_4 to decompose the materials and then converts the alkali sulfates to chlorides for the final precipitation of a suitable rubidium compound.(5-7) Smith's method(9) and its modifications(12-14) decomposes the rubidium-bearing material by heating it in a mixture of calcium carbonate and ammonium chloride. CO_2 and NH_3 are given off and the mixture reduces to lime and calcium chloride. Continued heating in this mixture converts most of the metals to low-solubility oxides while the calcium chloride sinters the mass. After cooling, the mass can be extracted with water; all of the alkali metals and a small portion of the calcium extract as chlorides. The calcium is removed from the mixture by precipitating it with ammonium carbonate and oxalate. Following filtration, the soluble rubidium (and other alkali metal) salts can then be converted to a suitable gravimetric compound.(5-7)

Barium, strontium, magnesium, borates, sulfates, and phosphates will interfere in either of these methods for the determination of rubidium and the other alkali metals. The removal of calcium by an ammonium carbonate and oxalate precipitation also removes barium and strontium.(15) Magnesium can be separated either by a precipitation of magnesium ammonium phosphate(16) or magnesium oxinate.(17) Borates can be volatilized from the chloride solution as methyl borates by adding methyl alcohol to the solution and evaporating the mixture to dryness.(15) Sulfate ions can be removed from the solution as $BaSO_4$ by adding barium chloride solution to the chloride mixture;(15) the excess barium can be removed by a precipitation with ammonium carbonate.(15) Precipitations, either with zinc carbonate(18) or with an $FeCl_3$ solution at a controlled pH,(15) will remove phosphates.

Rubidium may be separated from sodium and lithium by a precipitation as chloroplatinate or as perchlorate.(5) In the chloroplatinate method, the sodium and lithium chloroplatinates and the precipitating agent, H_2PtCl_6, are soluble in 80% ethyl alcohol and can be easily separated from the insoluble Rb_2PtCl_6. Several extractions of the chloroplatinate salts may be necessary to remove all of the lithium. Lithium chloroplatinate can also be used as the precipitating agent.(19) Potassium and cesium also form insoluble chloroplatinates and will interfere in this separation. If the chloroplatinates are precipitated from a nitrate solution with H_2PtCl_6, rubidium (and K and Cs) can be separated from large amounts of sodium, iron, aluminum, manganese, and other salts.(20) Quantitative separation of rubidium (and K and Cs) from the same elements can also be obtained by dissolving the chloroplatinates obtained by an H_2PtCl_6 precipitation from a chloride solution in 60-70% alcohol and a few drops of ethyl ether.(20) In the perchlorate method,(5) butyl alcohol - ethyl acetate and ethyl alcohol-0.2% $HClO_4$ mixtures have been used to extract the soluble sodium (and lithium) perchlorates from the insoluble perchlorate salts of K^{+1}, Rb^{+1}, Cs^{+1}, NH_4^{+1}, and Tl^{+1}. Sulfate ions must be absent because sodium sulfate is also insoluble in the solvents used for the extraction. Magnesium, the alkaline earths, nitrates, and phosphates do not interfere in the perchlorate method.

Rubidium can be separated from sodium, lithium, and many other elements by the trisodium cobaltinitrite method.(21-28) K^{+1}, NH_4^{+1}, Cs^{+1}, V^{+4}, U^{+6}, Sb^{+3}, Bi^{+3}, and Sn^{+4} interfere in this method. Rubidium can also be separated from large amounts of sodium by saturating an acid solution with gaseous hydrochloric acid(15) to produce NaCl.

Rubidium (and cesium) can be separated from potassium by precipitating them from a dilute HNO_3 solution with 9-phosphomolybdic acid.(20,29) Rubidium, potassium, and cesium can be separated from sodium and lithium by a chloroplatinic acid precipitation,(20,30-32) converted to the chlorides and the potassium separated by extracting the chloride mixture with absolute alcohol(33,34) saturated with hydrochloric acid gas. The rubidium and cesium chlorides are insoluble in this mixture. However, this method is a rather long and tedious one and it is sometimes necessary to re-extract the chlorides in order to remove all of the KCl. Depending upon the concentrations of all three elements, each element can interfere in the determination of the others.

2. <u>Separation By Electrolysis</u>. Although the alkali metals cannot be separated from solution by electrodeposition, their separation from other

elements can be effected by electrolysis with a mercury cathode at a controlled potential.(35) The alkali metals and the alkaline earth metals can be left in solution, while elements such as copper, cadmium, iron, cobalt, nickel, and zinc are deposited on the cathode. Specific separations of the metal, in this instance, rubidium, would have to be made from the electrolyzed solution.

3. Solvent Extraction Separations. Bock and Hoppe(36) have shown that the polyiodides of the alkali metals can be extracted with nitromethane. Their distribution ratios increase in the order Li < Na < K < Rb < Cs and are dependent upon the amount of free iodine added to the system.

Rubidium (and cesium) can be quantitatively extracted from a sodium tetraphenylboride, $NaB(C_6H_5)_4$, solution into nitrobenzene.(37) The use of 80% ethyl alcohol(19,20,30-32) to separate insoluble potassium (and Rb and Cs) chloroplatinates has already been reviewed above. Similarly, the use of butyl alcohol - ethyl acetate or ethyl alcohol - 0.2% $HClO_4$ mixtures inseparating the alkali perchlorates has already been discussed.(5) Additional information on this separation is given elsewhere.(38-42)

4. Chromatography Separations.

a. With Ion Exchange Resins. Cohn and Kohn(43) have used a Dowex-50 resin column and 0.15 N HCl as the eluate to separate Rb from Na, K, and Cs. Beukenkamp and Rieman(44) have also used Dowex-50 resin columns to separate Rb from the other alkalis. The separation was effected by using 0.70 N HCl as the eluant. Brooksbank, et al.,(45) and Kayas(46) have separated Rb from Na, K, and Cs by use of an Amberlite IR-100 resin colume. Na and K were eluted from the column with 0.1 N HCl and Rb separated from Cs with 1 N HCl. Kakihana,(47,48) in his studies on the preparation of KCl, has also used a cation resin column to separate rubidium from large amounts of KCl. Rubidium has also been separated from the other alkali metals contained in insoluble silicates by an ion exchange method.(49)

Lithium and sodium complexes of the chelating agent, ethylenediaminetetraacetic acid, EDTA, can be separated from Rb, K, and Cs, and from each other, by eluting an anion resin column of Dowex-1 (4% crosslinkage) with 0.13 M EDTA solution.(50)

b. By Paper Chromatography. A paper chromatographic technique using phenol saturated with 2 N HCl has been used for the purification of radioactive Rb^{86} from other radioelements.(51) The rate of Rb^{+1} movement upon a paper chromatogram has also been studied for solvent systems such as dipicrylamine in Na_2CO_3 solution,(52) alcohols in HCl,(53,54) alcohols in HNO_3,(55) ketones in HCl,(56) butanol-HBr,(57) and phenol.(55)

Rubidium has been separated from K and Cs by use of solvents composed of either conc. HCl-methanol-n-butanol-isobutylmethyl ketone,(58) or phenol saturated with 2 N HCl.(59) The alkali acetates can also be separated by paper chromatography using ethanol-2N acetic acid as a solvent.(60) Propanol-methanol mixtures as solvents have also been used to separate alkali hydroxide, citrate, and sulphate mixtures.(61-63)

Rubidium (and cesium) have been separated from potassium by using conc. HCl-methanol-n-butanol-isobutylmethyl ketone as a solvent(64) and by phenol saturated with 2 N HCl.(65)

In an electrolytic method, involving the placing of the paper chromatogram sprayed with phenolphthalien between two graphite electrodes for 5 seconds at a voltage of 6 volts, Kume, et al.,(66) have shown that Rb could be separated from the other alkali metals.

IV. DISSOLUTION OF SAMPLES CONTAINING RUBIDIUM

Most of the analytical methods used in determining rubidium and the other alkali metals require that they be collected as the chlorides. Most of the rubidium salts are readily soluble in water or dilute acid; most metals and alloys containing rubidium can be put into solution with acids such as HCl, HNO_3, HF, or a combination of these acids.

Some rocks and minerals are soluble in HCl. However, when the rock or mineral is not acid soluble, either the Berzelius method(8) or the Smith method(9) can be used to dissolve the sample. In the Berzelius method(8) the rock is attacked with HF and H_2SO_4 and the excess fluorine and silicon removed by a distillation, followed by a removal of all metals except the alkalies. The alkali sulfates are then converted to chlorides. In the Smith method,(9) the powdered rock is heated with a mixture of ammonium chloride and calcium carbonate. Under these conditions, the alkali metals are converted to chlorides which can be extracted by water.

Soils can be decomposed by treatments with ammonium acetate, HCl, and aqua regia,(67,68) or by leachings with either HNO_3,(69) HCl-HF,(70) and H_2SO_4.(71) Biological materials, such as tissues, body fluids, vegetation, etc., can be decomposed with HCl, HNO_3, HNO_3-H_2SO_4, or HNO_3-$HClO_4$ mixtures.(67,68)

If any of these dissolution techniques are used in a radiochemical separation of the rubidium radionuclides, the addition of inactive <u>rubidium carrier</u> to the mixture before decomposition begins would greatly assist in achieving an isotopic exchange between the radioactive and inactive rubidium atoms. The exchange should be rapid and complete, since rubidium exists in only one oxidation state.

V. SAFETY PRACTICES

The solubilization and the processing of any material by chemical means inherently can be hazardous. In any analysis for an alkali metal, it should be noted that some of the inactive alkali metal compounds can be extremely toxic and should be treated carefully. Likewise, some of the reagents used in decomposing a sample and completing an analysis can be harmful. Thus, adequate safety precautions should be followed in processing any sample material. Pieters and Creyghton's manual(72) on safe laboratory practices, as well as others on laboratory safety, should be consulted before any analysis is undertaken.

The processing of a radioactive material in a laboratory area greatly magnifies the needs for safe laboratory practices. If radioactivity is discharged into a laboratory area by evolution or spillage, hazardous conditions for personnel and widespread contamination can result. Safety practices followed in the processing of radioactive materials appear in such sources as the Oak Ridge National Laboratory's Master Analytical Manual(73) and in the International Atomic Energy Agency's publication, entitled, "Safe-Handling of Radioisotopes."(74) Many other similar sources of information exist and should be consulted.

VI. COUNTING TECHNIQUES FOR THE RADIOACTIVE RUBIDIUM ISOTOPES

The nuclear characteristics of the radioactive isotopes of rubidium are summarized in Table I of this monograph. Rubidium has a naturally occurring radioactive isotope, Rb^{87}. Rb^{87} decays with half-life of 6×10^{10} years.

Rubidium radioisotopes most frequently measured are Rb^{86} (19.5 d) and Rb^{88} (17.8 m). Counting techniques such as Geiger-Mueller counting, proportional counting, or gamma scintillation spectrometry(75-79) are used in measuring the radioactivity of these radioisotopes. Generally, a sample material must be processed radiochemically before any of these radioactivity measurements can be made. However, it should be possible to determine either of these rubidium isotopes by a nondestructive gamma scintillation spectrometry method.(79)

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR RUBIDIUM RADIONUCLIDES

The radiochemical procedures that now exist for the determination of the rubidium radionuclides have evolved from ideas and techniques similar to those reported in Section III of this monograph and reflect on the requirements of each investigation that has been undertaken. Both carrier-free and carrier separation techniques have been employed.

An ion-exchange method has provided carrier-free rubidium radioactive tracer.(45) The solvent extraction separations, as well as the chromatography methods reported in Section III above, suggest possible carrier-free separations for the radioactive rubidium isotopes.

Carrier methods have also been used in the preparation of radioactive rubidium tracers(80) and separating them from fission products.(81) In addition, carrier methods of radiochemical analysis have been used to determine rubidium by radioactivation analysis.(82,83) The procedures that have been used in the radioactivation analysis determination of trace rubidium in water,(84,85) vegetation,(84) alkali metals,(86) meteorites,(87) minerals,(87,88) rocks,(87,89) alkali metal salts,(45,84) sodium-potassium alloys,(90) and sea water (89,91) are given in some detail in this section.

Each radiochemical procedures that follows gives information about the procedure's use, type of nuclear bombardment, type material analyzed, separation time, etc. In addition, available information regarding the ease with which the rubidium isotopes can be separated from other radioactivities is presented.

PROCEDURE 1

Procedure Used In: Radioactivation analysis

Method: Ion Exchange (carrier-free separation)

Element Separated: Rb^{86} (19.5 d)

Type Material Analyzed: Alkali carbonates and chlorides,(45,84) water,(84) and vegetation.(84)

Type Nuclear Bombardment: $Rb^{85}(n,\gamma)Rb^{86}$

Procedure By: Brooksbank and Leddicotte(45) (Reported in detail by Leddicotte(84)

Separation Time: Several hours

Chemical Yield of Carrier: A carrier-free separation

Decontamination: Excellent from radionuclides of Na, K, and Cs.

Equipment Required: Ion exchange columns

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 1) and comparator samples (Note 2) in a neutron flux of at least 6.5×10^{11} n/sec/cm^2 for 16 hours or longer (Note 3). Prepare the test and comparator samples for the irradiation either by wrapping each specimen in aluminum foil or placing it in a quartz ampoule. If the sample is a liquid, small polyethylene bottles can be used to contain the sample during the irradiation (Note 4).

B. Preparation of Irradiated Materials for Analysis.

I. The Comparator Sample

1. After the irradiation, quantitatively transfer the comparator sample (Note 2) to a 100-ml volumetric flask. Dissolve the sample in a small measured

volume of distilled water; then dilute the solution to 100 ml with water. Mix the solution thoroughly by shaking it carefully.

2. By means of a 1-ml volumetric pipet, transfer an aliquot to a second 100-ml volumetric flask; then dilute the aliquot to 100 ml with water.

3. Shake the solution thoroughly; then pipet an aliquot of this solution directly to the top of the ion-exchange column (Notes 5 and 6). Then proceed in the manner described below in Step 1 of Part C.

II. Solid Test Samples

1. If the sample is a solid, quantitatively transfer the test portion into a 50-ml glass centrifuge tube, and then add dropwise to the same centrifuge tube enough concentrated HCl to completely dissolve the sample. If necessary, heat the mixture to dissolve the sample. Transfer the solution of the irradiated sample to the top of the ion-exchange column (Notes 5 and 6). Then continue with Step 1 of Part C below.

III. Liquid Test Samples

1. Pipet an aliquot of the irradiated test portion directly on to the top of the ion-exchange column (Notes 5 and 6); then continue with Step 1 of Part C below.

C. Ion Exchange Separation of Rubidium

1. Connect the ion-exchange column to a reservoir (Note 7) that contains a supply of 0.1 $\underline{M}$ HCl. Adjust the flow rate so that the eluate flows from the column at the rate of 1 ml per minute.

2. Continue the flow of the 0.1 $\underline{M}$ HCl through the column and collect and discard the first 400 ml of eluate that passes through the column (Note 8).

3. Collect the next 500 ml of eluate and discard (Note 9).

4. Collect the next 700 ml of eluate and discard (Note 10).

5. Allow the flow of the eluate to continue until an additional 800 ml has been collected in a new collection vessel (or series of beakers). Process this fraction of the eluate as instructed in Step 1 of Part D below.

6. If cesium is not to be determined, stop the flow of eluate from the column after this collection (Note 11).

D. Preparation of Rb^{86} Eluate For Radioactivity Assay

1. Evaporate to dryness the solution that was collected in Step 5 of Part C above. Add 1 to 2 ml of conc. HCl to the beaker, and then wash the solution into a 10-ml volumetric flask. Rinse the beaker with small portions of H_2O, transfer the rinsings to the flask, and dilute the solution to volume. Assay the solution for Rb^{86} radioactivity as instructed in Part E below.

E. Measurement of Rb^{86} Radioactivity and Calculation of Stable Rubidium Content of Test Sample

1. The Rb^{86} radioactivity in both the test and comparator samples may be assayed by beta or gamma counting. Use a Geiger-Mueller counter for the beta measurements and a gamma scintillation counter for the gamma measurements (Note 12).

2. Following the radioactivity measurements, correct the observed Rb^{86} radioactivity for decay (Note 13), dilution volume(s), and the sample weights (or volumes) of both the test and comparator samples. A simple ratio of these corrected radioactivities becomes a measurement of the amount of stable rubidium in the test sample:

$$\%\ \text{Rb in Test Sample} = \frac{\text{Corrected Rb}^{86}\ \text{radioactivity in Test Sample}}{\text{Corrected Rb}^{86}\ \text{radioactivity in Comparator Sample}} \times 100$$

Notes:

1. Use at least 0.1-0.2 gram portions.

2. Use from 0.025 to 0.030 gram of rubidium carbonate.

3. The limits of measurement for this procedure is about 0.05 micrograms of rubidium.

4. This type of sample will have to be irradiated in an air-cooled or water-cooled facility of the reactor.

5. The ion exchange column is composed of 100- to 120-mesh IR-1 (or Ir-100) resin packed into a glass column 1 cm in diameter and 100 cm long. A small glass wool plug at the base of the column holds the resin in the column. The resin is pretreated with a solution of 0.1 M HCl. The treatment consists of

passing the 0.1 M HCl solution over the column until the desired molarity (0.1 M) is obtained.

6. The transfer may be made by use of a volumetric pipet. If it is necessary to rinse the pipet, use 0.1 M HCl as the rinse liquid. In transferring the radioactive solution on to the column, exercise care in delivering the solution from the pipet so that the resin at the top of the column will not be disturbed.

7. A dispensing bottle of at least 3-liter capacity is suitable for use as a reservoir. Tygon or rubber tubing may be used to connect the reservoir to the column.

8. This solution may contain radioactive anionic constituents as well as separated Na^{24} (15 h) radioactivity; the presence of these should not be confused with K^{42} or Rb^{86} which are eluted later.

9. This particular procedure is designed to separate Na, K, Rb, and Cs in alkali carbonates and chlorides. This fraction will contain Na^{24} (15 h), and it can be processed for the amount of stable sodium in the sample, if a sodium comparator sample has been used in the irradiation.

10. This fraction will contain K^{42} (12.8 h), and it can be processed for the amount of stable potassium in the sample, if a potassium comparator sample has been used in the irradiation.

11. If Cs is to be determined, continue as follows: Strip the column with at least 1 N HCl and process this fraction for Cs. Cesium comparator samples should have been irradiated, if stable Cs is to be determined in a sample.

12. Gamma-ray energy discrimination may be used here.

13. Decay measurements may be followed, if required.

PROCEDURE 2

Procedure Used In: Preparation of radioactive tracers

Method: Precipitation

Element Separated: Rb^{86} (19.5 d)

Type Material Bombarded: Bismuth

Type of Nuclear Bombardment: 184" cyclotron (388-Mev alphas; 348-Mev protons; 194-Mev deuterons)

Procedure By: Goeckermann (Reported by Meinke(80))

Separation Time: Several hours

Chemical Yield of Carrier: ~ 30%

Decontamination: 10^3

Equipment Required: Standard

Procedure:

1. To aliquot of HNO_3 solution of target, add 20 mg Rb and Cs and 5 ml conc. $HClO_4$. Evaporate to fuming, cool, transfer to centrifuge tube with 15 ml absolute EtOH. Cool in ice bath 10 min. with stirring. Wash ppt twice with 10 ml absolute EtOH.

2. Dissolve in dilute HCl and scavenge with Te, Ru, Sn, Sb, and Ag sulfides (2 mg each) by adding H_2S.

3. Scavenge with NH_3 pptn of La, Ce, Y, Zr, and Cb (2 mg each).

4. Scavenge with Sr and Ba carbonates (4 mg).

5. Acidify with HCl, repeat (2).

6. Repeat (3).

7. Scavenge with $La(OH)_3$.

8. Scavenge with Sr and Ba carbonates and Y, Zr, and Cb hydroxides.

9. Acidify with HCl, evaporate to dryness in a Pt dish, destroy NH_4Cl by adding a few drops HNO_3 and baking carefully (do not overheat or Cs may be lost).

10. Dissolve in a minimum of H_2O, transfer to a cone and centrifuge out any residue, evaporate to dryness in the cone. Add 6 ml H_2PtCl_6 and 6 ml EtOH, wash Rb and Cs chloroplatinates with EtOH.

11. Dissolve in HCl and repeat Te sulfide scavenging.

12. Repeat NH_3 pptn of La and Fe hydroxides.

13. Repeat Sr and Ba carbonate scavenge.

14. Acidify with HNO_3, add HCl, evaporate to dryness, bake off ammonium salts carefully again.

15. Cs - Take up residue in 20 ml 6 N HCl, add 1 ml silicotungstic acid solution and digest. (Save this supernate for Rb fraction).

16. Rb - Ppt a Cs silicotungstate scavenge from the supernate saved. Evaporate until crystallization begins, add H_2PtCl_6 and EtOH, filter, wash with EtOH, dry 10 minutes at 110° C. Weigh as Rb_2PtCl_6 (33.9 mg per 10 mg Rb).

PROCEDURE 3

Procedure Used In: Preparation of radioactive tracers

Method: Precipitation

Element Separated: Rb^{86} (19.5 d)

Type Material Bombarded: NH_4Br

Type of Nuclear Bombardment: 40-140 Mev alphas

Procedure By: Karraker (Reported by Meinke(80))

Separation Time: ~ 30 minutes

Chemical Yield of Carrier: ~ 40%

Decontamination: 10^2

Equipment Required: Standard

Procedure:

1. NH_4Br in porcelain crucible, add a few drops of dilute HCl, then heat strongly in hood, using burner, NH_4Br sublimes off, Kr activities evaporate. Continue heating until no more solid is visible. Wash crucible with a small amount of dilute HNO_3. (For mass spectrographic purposes, this is sufficiently pure).

2. Add about 1 mg Rb carrier, and scavenge the solution with few mg of $Te(OH)_3$, $MgCO_3$, AgCl, and any sulfide. This, practically speaking, removes all impurities except alkalis.

PROCEDURE 4

Procedure Used In: Preparation of radioactive tracers

Method: Precipitation

Element Separated: Rb^{86} (19.5 d)

Type Material Bombarded: $SrClO_4$ (tracer or with 50 micrograms of carrier) in 10 $\underline{M}$ $HClO_4$.

Type of Analysis: Milking Experiment

Procedure By: Castner (Reported by Meinke(80))

Separation Time: 20 minutes

Chemical Yield of Carrier: ~ 50%

Decontamination: Less than 2% Sr carried along

Equipment Required: Standard

Procedure:

1. Solution is heated in boiling H_2O. (Solution volume = 1 ml.) 50 μ gms $RbNO_3$ are added. Stir.

2. Cool in ice bath and let stand for 5 minutes. Centrifuge and remove supernatant for later milking. (The $RbClO_4$ may be dissolved in any solution if heated.)

3. Add 250 λ saturated $Na_2C_2O_4$ solution, and heat until just dissolved.

4. Add 50 μ gms Sr^{++} solution and centrifuge the ppt while the solution is still hot.

5. The supernatant containing the Rb is then removed.

PROCEDURE 5

Procedure Used In: Separation of Rb^{86} from fission product mixtures

Method: Precipitation

Element Separated: Rb^{86} (19.5 d)

Type Material Bombarded: Uranium

Type of Nuclear Bombardment: n,fission

Procedure By: Stanley (Reported by Kleinberg(81))

Separation Time: Several hours

Chemical Yield of Carrier: Quantitative

Decontamination: Radiochemically purity possible

Equipment Required: Standard

Procedure:

1. Pipet 5 ml of the Rb carrier solution into a 125-ml Erlenmeyer flask. Add the sample and then 5 ml of conc. HNO_3 and 8 ml of 70% $HClO_4$. Add 4 drops each of Ba and Sr holdback carriers. Boil the solution to dense, white fumes, cool to room temperature, and transfer to a 40-ml conical centrifuge tube with 20 ml of absolute ethanol. Cool in an ice bath for 10 min. and centrifuge (Note 1). Wash the $RbClO_4$ precipitate twice with 10-ml portions of absolute ethanol, discarding the washings.

2. Dissolve the $RbClO_4$ in 10 ml of H_2O by heating nearly to boiling. Add 4 drops of Fe carrier and 2 drops of phenolphthalein indicator solution. Add 6 M NH_4OH until the solution is basic. Centrifuge and transfer the supernate to another centrifuge tube, discarding the precipitate. Repeat the $Fe(OH)_3$ precipitation two additional times.

3. To the supernate add 1 ml of Ba carrier and 4 drops of Sr carrier. Add 1 ml of 2 M Na_2CO_3 and centrifuge. Transfer the supernate into another centrifuge tube which contains 1 ml of Ba carrier and 4 drops of Sr carrier. Centrifuge and decant into a 125-ml Erlenmeyer flask, discarding the precipitate.

4. Add 2 drops of 6 M NaOH and heat to boiling. Make certain that all the NH_3 is boiled out and add 5 ml of 6 M HNO_3 and 8 ml of $HClO_4$. Boil to white fumes, cool to room temperature, and transfer to a centrifuge tube with 20 ml of absolute ethanol. Cool in an ice bath for 10 min and centrifuge, decanting the supernate into running H_2O. Wash the $RbClO_4$ precipitate twice with 10-ml portions of absolute ethanol.

5. Dissolve the $RbClO_4$ in 7 ml of H_2O and add 1 ml of Cs carrier solution. Heat nearly to boiling and add 3 ml of BiI_3-HI reagent. Cool in an ice bath and centrifuge the $Cs_3Bi_2I_9$ precipitate. Decant the supernate into another centrifuge tube and discard the precipitate. Add 1 ml of BiI_3-HI reagent, heat nearly to boiling, and add 1 ml of Cs carrier. Cool in an ice bath and

centrifuge. Repeat four additional times for a total of six precipitations of $Cs_3Bi_2I_9$. Before the final centrifugation, add a drop or two of aerosol solution. Decant the final supernate into a 125-ml Erlenmeyer flask.

6. Boil the solution nearly to dryness. Add 2 ml of conc. HNO_3 and boil off the I_2 which forms. Boil the solution to dryness and add 5 ml of conc. HCl. Boil again to dryness and again add 5 ml of conc. HCl. Boil to dryness. Add 1 ml of conc. HCl and transfer to a centrifuge tube with 20 ml of H_2O. Precipitate Bi_2S_3 by passing in H_2S gas. Add a drop of aerosol and centrifuge. Decant the supernate into a 125-ml Erlenmeyer flask and discard the precipitate.

7. Add 5 ml of conc. HCl and boil out the H_2S. Add 5 ml of conc. HNO_3 and 8 ml of $HClO_4$ and boil to dense, white fumes. Cool to room temperature and transfer to a centrifuge tube with 20 ml of absolute ethanol. Cool in an ice bath for 10 min. and centrifuge. Pour the supernate into running H_2O. Wash the precipitate twice with 10-ml portions of absolute ethanol.

8. Add to the precipitate of $RbClO_4$, 15 ml of $SnCl_4$ reagent. Heat on a steam bath for a few minutes, stirring occasionally to insure conversion of the $RbClO_4$ to Rb_2SnCl_6. Centrifuge and discard the supernate.

9. Dissolve the Rb_2SnCl_6 in 20 ml of H_2O by heating. Pass in H_2S to precipitate SnS_2. Centrifuge and decant the supernate into a 125-ml Erlenmeyer flask, discarding the precipitate. Add 5 ml of conc. HCl and boil nearly to dryness. Transfer to a centrifuge tube with 5 ml of H_2O and again pass in H_2S. Centrifuge and transfer the supernate to a 125-ml Erlenmeyer flask.

10. To the supernate add 5 ml of conc. HCl and boil out the H_2S. Add 5 ml of conc. HNO_3 and 8 ml of $HClO_4$ and boil to dense, white fumes. Cool to room temperature and transfer to a centrifuge tube with 20 ml of absolute ethanol. Cool in an ice bath for 10 min. and centrifuge. Discard the supernate in running H_2O.

11. To the precipitate add 5 ml of saturated sodium hydrogen tartrate and about 250 mg of solid sodium hydrogen tartrate. Heat until solution

occurs. Cool to room temperature and allow to stand for 1/2 hour. Centrifuge and discard the supernate.

12. Dissolve the precipitate by heating with 5 ml of H_2O and transfer to a 125-ml Erlenmeyer flask. Add 10 ml of conc. HCl, 5 ml of conc. HNO_3, and 8 ml of $HClO_4$. Warm and set on a steam bath for a few minutes. Boil until the NO_2 fumes disappear and add a few drops of HNO_3 (Note 2). Boil until dense, white fumes appear, and cool to room temperature. Transfer to a centrifuge tube with 20 ml of absolute ethanol and cool for 10 min. in an ice bath. Centrifuge and discard the supernate into running H_2O. Wash twice with 10-ml portions of absolute ethanol.

13. Dissolve the $RbClO_4$ by heating with 5 ml of H_2O and transfer to a 125-ml Erlenmeyer flask. Boil out the ethanol and add 5 ml of conc. HNO_3 and 8 ml of $HClO_4$. Boil until dense, white fumes appear. Cool to room temperature and transfer to a centrifuge tube with 20 ml of absolute ethanol. Cool for 10 min. in an ice bath and centrifuge, pouring the supernate into running H_2O. Wash twice with 10-ml portions of absolute ethanol (Note 3). Slurry the precipitate in 5 ml of absolute ethanol and filter on a weighed Whatman 42 filter paper disk, 7/8" diameter, using a ground-off Hirsch funnel and a filter chimney. Wash down the sides of the funnel with small portions of absolute ethanol. Dry at 110° C for 15 min., cool for 10 min., and weigh. Mount and count immediately (Note 4).

Notes:

1. If it is necessary to save this supernate for recovery of uranium, pour into 50 ml of H_2O in a beaker and set aside. Otherwise, pour immediately into running H_2O to decompose the explosive ethyl perchlorate which will have formed.

2. This is a step requiring considerable caution. The tartrate occasionally does not decompose until it is in the hot $HClO_4$ solution in which case there is danger of explosion. If the solution suddenly turns black during heating, quickly add 1 to 2 ml of conc. HNO_3 to oxidize the organic material.

3. The $RbClO_4$ precipitate must be washed thoroughly with ethanol to remove $HClO_4$. If this is not done, the filter paper will char on drying.

4. Since 19.7 d Rb^{86} is a shielded isotope formed in very low yield, the counts will be very low. Therefore, a low background counter is recommended.

PROCEDURE 6

Procedure Used In: Radioactivation analysis

Method: Precipitation

Element Separated: Rb^{86} (19.5 d)

Type Material Bombarded: Water(85)

Type of Nuclear Bombardment: $Rb^{86}(n,\gamma)Rb^{88}$

Procedure By: Blanchard, Leddicotte, and Moeller(85)

Separation Time: Several hours

Chemical Yield of Carrier: 60-70%

Equipment Needed: Standard

Procedure:

1. 30 mls of water were placed in a polyethylene bottle and irradiated for 16 hours in a flux of 6.5×10^{11} n/cm^2/sec.

2. If any specific element, such as rubidium, is to be analyzed quantitatively, a known amount of Rb_2CO_3 is irradiated along with the water sample. The standard is processed in the same manner as the unknown sample.

3. The radiochemical separation is carried out as outlined in "The Chemical Separation Scheme" attached.

4. The rubidium is found in the last step (Part II of the "Scheme") as the Soluble Group along with sodium, potassium, and cesium. Because of the Na^{24} (15 d) gammas, a further separation of these elements are made by forming the perchlorates and dissolving the sodium perchlorate in a

mixture of butyl alcohol and ethyl acetate, Rubidium and potassium perchlorates are insoluble under these conditions.

5. The radioactivity of either the "Soluble Group" or the insoluble perchlorates is analyzed by gamma scintillation spectrometry. K^{42} decays with gamma radiations of 1.51 Mev and a half-life of 12.8 h; Rb^{86} decays with gamma radiations of 1.054 Mev (Note 1).

6. Following the radioactivity measurements, correct the observed Rb^{86} radioactivity for decay, dilution volume, sample and yield weights for both the sample and standard. A ratio of these corrected radioactivities becomes a measurement of the amount of stable rubidium in the water sample:

$$\%\ \text{Rb in } H_2O \text{ sample} = \frac{\text{Corrected } Rb^{86} \text{ radioactivity in } H_2O \text{ sample}}{\text{Corrected } Rb^{86} \text{ radioactivity in standard sample}} \times 100$$

Note:

1. A decay study will assist in resolving the interference of K^{42} in the measurement of Rb^{86}.

Chemical Separation Scheme

1) Add the radioactive sample to a 50 milliliter centrifuge tube. Aerate to remove radioactive gases. Acidify with HNO_3 and add Cl, Br, I, Cu, As, Fe, Y, Co, Mn, Zn, Ba, Sr, Ca, Na, and K carriers. Precipitate Cl, Br, and I with slight excess of Ag. Heat to coagulate the precipitate. Centrifuge.

2) Precipitate: AgCl, AgBr, AgI. Wash with water, filter, mount and count. Designate as the SILVER GROUP.

3) Supernate: Adjust acidity to 0.5 N HCl. Saturate with H_2S. Centrifuge.

4) Precipitate: $CuS + As_2S_3$. Wash with water, filter, mount and count. Designate as the ACID SULFIDE GROUP.

5) Supernate: Transfer to beaker. Add 1 ml conc. HCl. Boil until solution is clear. Oxidize Fe^{++} to Fe^{+++} by boiling with HNO_3. Cool solution and make 1:1 with conc. HCl. Neutralize with conc. NH_4OH to precipitate hydroxide. Centrifuge.

6) Precipitate: Fe + Y hydroxides. Wash with water, filter, mount and count. Designate as the HYDROXIDE GROUP.

7) Supernate: Saturate with H_2S. Centrifuge

8) Precipitate: CoS, MnS, ZnS. Wash with water, filter, mount and count. Designate as the BASIC SULFIDE GROUP.

9) Supernate: Acidify solution with HCl. Boil to remove H_2S. Add $(NH_4)_2H(PO_4)$ and an excess of NH_4OH. Digest. Centrifuge.

10) Precipitate: Ca, Ba, and Sr phosphates. Wash, filter, mount, and count. Designate as the ALKALINE GROUP.

11) Supernate: Soluble ions. Designate as the SOLUBLE GROUP.

PROCEDURE 7

Procedure Used In: Radioactivation analysis

Method: Ion Exchange (a carrier separation)

Element Separated: Rb^{86} (19.5 d)

Type Material Analyzed: Rocks, Minerals, and Meteorites(87-89)

Type Nuclear Bombardment: $Rb^{85}(n,\gamma)Rb^{86}$

Procedure By: Cabell and Smales(87)

Separation Time: Several hours

Chemical Yield of Carrier: Quantitative

Decontamination: Excellent from radionuclides of Na, K, and Cs.

Equipment Required: Ion exchange columns

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 1) and comparator samples (Note 2) in a neutron flux (Note 3). Prepare the test and comparator samples for the irradiation, placing each specimen in a sealed silica tube.

B. Preparation of Irradiated Materials for Analysis

1. After the irradiation, add the sample to a mixture of RbCl (40 mgs) in a platinum crucible and cover with 4-5 g of Na_2O_2. Heat the crucible for 1 hour at 470° C. Cool, then dissolve sinter in small amount of water. Then add 2 ml of a ferric chloride and 6 M NaOH dropwise until ferric hydroxide precipitates. Centrifuge; discard ppt.

2. To the supernatant liquid add sufficient acetic acid to acidify it; then, add 10 ml of 10% sodium cobaltinitrite solution. Digest the mixture for 5 minutes in an ice bath. Centrifuge; discard the supernatant liquid.

3. Dissolve the cobaltinitrate precipitate in 2 ml of 1:1 HNO_3. Evaporate to dryness. Then, dissolve the residue in 5 ml and transfer the solution to the top of an ion-exchange column (Notes 4 and 5). Then continue with Step 1 of Part C below.

C. Ion Exchange Separation of Rubidium

1. Connect the ion-exchange column to a reservoir (Note 6) that contains a supply of 0.1 M HCl. Adjust the flow rate so that the eluate

flows from the column at the rate of 2.5 ml per minute.

2. Continue the flow of the 0.1 M HCl through the column and collect and discard the first 700 ml of eluate that passes through the column (Note 7).

3. Allow the flow of the eluate to continue until an additional 100 ml has been collected in a second collection vessel. Process this fraction of the eluate as instructed in Step 1 of Part D below.

4. If cesium is not to be determined, stop the flow of eluate from the column after this collection (Note 8).

D. Preparation of Rb^{86} Eluate for Radioactivity Assay

1. Evaporate to dryness the solution that was collected in Step 3 of Part C above. Dissolve the residue in water, make the solution alkaline with NaOH, neutralize with alkali-metal cobaltinitrite. Collect the precipitate by filtration.

2. Dissolve cobaltinitrite precipitate in HNO_3. Then add ethanol and a solution of hexachloroplatinic acid. Wash the hexachloroplatinic acid precipitate; transfer to a weighed counting tray and then dry under an infrared lamp and weigh.

E. Measurement of Rb^{86} Radioactivity and Calculation of Stable Rubidium Content of Test Sample

1. The Rb^{86} radioactivity in both the test and comparator samples may be assayed by beta counting. Use a Geiger-Mueller counter for the beta measurements.

2. Following the radioactivity measurements, correct the observed Rb^{86} radioactivity for decay, dilution volume(s), and the sample weights (or volumes) of both the test and comparator samples. A simple ratio of these corrected radioactivities becomes a measurement of the amount of stable rubidium in the test sample:

$$\%\ \text{Rb in Test Sample} = \frac{\text{Corrected } Rb^{86} \text{ radioactivity in Test Sample}}{\text{Corrected } Rb^{86} \text{ radioactivity in Comparator Sample}} \times 100$$

Notes:

1. Use at least 0.01 to 0.25 gram portions.

2. Use from 0.10 to 0.20 gram of rubidium chloride solution.

3. In this instance, the "self-serve" or "rabbit" positions of the Harwell Pile are used for periods up to 4 weeks.

4. The ion exchange column is composed of "normal" grade Zeo-Karb 315 ion exchange resin packed into a glass column 3.8 cm in diameter and 100 cm long. A small glass wool plug at the base of the column holds the resin in the column. The resin is pretreated with a solution of 3.0 M HCl. The treatment consists of passing 24 liters of 3.0 M HCl solution over the column to convert it to the hydrogen form.

5. Use water as a rinse and for transfer to the column. Use separate columns for the test and comparator samples.

6. A dispensing bottle is suitable for use as a reservoir. Tygon or rubber tubing may be used to connect the reservoir to the column.

7. This eluate volume may contain radioactive anionic constituents as well as separated Na^{24} (15 h) and K^{42} radioactivity; the presence of these should not be confused with Rb^{86} which is eluted later.

8. If Cs is to be determined, continue as follows. Strip the column with at least 150 ml of 1 N HCl and process this fraction for Cs. Cesium comparator samples should have been irradiated, if stable Cs is to be determined in a sample.

PROCEDURE 8

Procedure Used In: Radioactivation analysis

Method: Precipitation

Element Separated: Rb^{86}

Type Material Bombarded: Alkali metals,(86) metal salts,(90) sodium-potassium alloys,(90) and sea water(91)

Type Nuclear Bombardment: $Rb^{85}(n,\gamma)Rb^{86}$

Procedure By: Smales and Salmon(91)

Separation Time: A few hours

Chemical Yield of Carrier: Quantitative

Equipment Needed: Standard

Procedure:

A. Irradiation of Sample Material

1. Each sample was irradiated for periods between a few hours and 2 days in the Harwell reactor. Portions of a rubidium salt was used as a standard.

B. Radiochemical Separation of Rb^{86}

1. After the irradiation, dissolve sample in a mineral acid (HCl) in the presence of 50 mg of Rb carrier. Add ferric chloride (in solution) and 6 M NaOH solution. Centrifuge and discard the precipitate.

2. Acidify the supernatant liquid with glacial acetic acid and add an excess of 10% aqueous sodium cobaltinitrite. Mix well.

3. Then centrifuge the slurry. Discard the supernatant liquid. Wash the precipitate 3 times with water. Discard the washes after centrifuging.

4. Dissolve the cobaltinitrite precipitate in 1:1 HNO_3; boil, then cool and add 15 ml of ethanol. Precipitate rubidium chloroplatinate by the addition of 1 ml of 10% w/v platinum chloride solution. Centrifuge; discard the supernatant liquid.

5. Transfer the chloroplatinate precipitate to a counting tray, dry under an infrared lamp. Cool and weigh.

6. The Rb comparator is carried through the same procedure as each test sample.

C. Measurement of Rb^{86} Radioactivity

1. The activity of the Rb^{86} may be measured by beta counting. Use a Geiger-Mueller counter for beta measurements.

2. Following the radioactivity measurements, correct the Rb^{86} activity for decay, dilution volume, and sample and yield weights for both the test and comparator samples. A ratio of these corrected radioactivities becomes a measurement of the stable rubidium in the sample:

$$\% \text{ Rb in Sample} = \frac{\text{Corrected } Rb^{86} \text{ in Mg sample}}{\text{Corrected } Rb^{86} \text{ in standard sample}} \times 100$$

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