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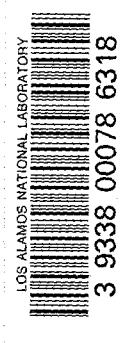
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The Radiochemistry of Potassium



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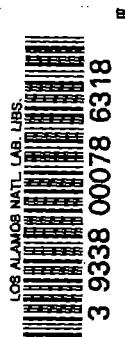
CHEMISTRY

The Radiochemistry of Potassium

W. T. MULLINS AND G. W. LEDDICOTTE

*Oak Ridge National Laboratory
Oak Ridge, Tennessee*

November 1961



Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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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 potassium 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 potassium which might be included in a revised version of the monograph.

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The Radiochemistry of Potassium

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

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II. RADIOACTIVE NUCLIDES OF POTASSIUM

The radioactive nuclides of potassium that are of interest in the radiochemistry of potassium 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⁾

TABLE I
THE RADIOACTIVE NUCLIDES OF POTASSIUM

<u>Radio-Nuclide</u>	<u>Half-Life</u>	<u>Mode of Decay</u>	<u>Energy of Radiation</u>	<u>Produced By</u>
K ³⁷	1.3 s	β^+	$\beta^+ 4.6$	K- γ -2n
K ³⁸	7.7 m	β^+	$\beta^+ 2.8$ $\gamma 2.16$	Cl- α -n, K-n-2n, K-p-pn K- γ -n, Ca-d- α
K ⁴⁰	1.32×10^9 y	β^-	$\beta^- 1.33$ $\gamma 1.46$ 1.55	Natural source
K ^{41m}	6.7×10^{-9} s	π^-	$\gamma \sim 1.3$	Daughter A ⁴¹
K ⁴²	12.4 h	β^-	$\beta^- 3.58$ $\gamma 1.51$	A- α -pn, K-d-p, K-n- γ Ca-n-p, Sc-n- α
K ⁴³	22.4 h	β^-	$\beta^- 0.81, 0.24$ $\gamma \sim 0.4$	A- α -p
K ⁴⁴	17 m.	β^-		Ca-n-p

III. THE CHEMISTRY OF POTASSIUM AND ITS APPLICATION IN ANALYSIS METHODS FOR THE POTASSIUM RADIONUCLIDES

Radiochemical analysis methods usually follow the ideas and techniques established by more conventional analysis methods to determine a non radioactive element in an inactive sample material. Since these methods - precipitation, solvent extraction, chromatography, and electrolysis - are dependent upon chemical reactions to bring them to completion, the general information given below on the formation of potassium compounds and their behavior in separation methods is intended to establish the usefulness of such ideas and techniques in analyzing a radioactive (or nonradioactive) material for the potassium radionuclides.

A. The General Chemistry of Potassium

The earth's crust contains at least 2.5% potassium. Potassium compounds are found in soils, sea water, mineral water, igneous rocks and minerals. The

chief mineral sources of potassium are carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$; polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$; sylvite, KCl ; silvinit, a mixture of KCl and $NaCl$; schönlite, $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$; and kainite, $MgSO_4 \cdot MgCl_2 \cdot K_2SO_4 \cdot 6H_2O$.

Potassium metal is usually produced by an electrolytic process in which an aqueous solution of the mineral is electrolyzed and the insoluble impurities, such as $Mg(OH)_2$ are filtered off. The solution of KCl remaining after this filtration is further electrolyzed to produce a solution of KOH . The KOH solution is then evaporated to dryness and elementary potassium obtained by an electrolysis of the fused KOH .

1. Metallic Potassium

Potassium metal is a soft, silver-white metal having a density of 0.86. Potassium is composed of three isotopes: K^{39} (93.1%), K^{40} (0.1%), and K^{41} (6.8%). K^{40} is a naturally occurring radioactive isotope having a half-life of 10^9 years. Potassium will melt at 62° and it has a boiling point of 760° .

Potassium metal rapidly develops an oxide coating if it is exposed to air. It will react with water to form hydrogen and solutions of the corresponding bases. It will combine with hydrogen to form a hydride. Most of its salts are very soluble in water. It will dissolve in ammonia to form a blue solution and when it is volatilized, a blue vapor composed of monatomic molecules is given off.

2. The Chemical Compounds of Potassium

Potassium has only a +1 oxidation state. It is more active towards the non-metals than is sodium; however, its chemical properties are similar to sodium. It will react with carbon dioxide, hydrogen, oxygen, nitrogen, sulfur, and the halogens. The reactions of potassium with these and other elements is presented in some detail below. Table II shows the solubility of many of the potassium compounds in water and other reagents.

a. Potassium Hydride, KH. Potassium will combine directly with hydrogen on heating to form KH. The colorless crystals of KH decompose rapidly on heating and will react with water to produce hydrogen gas.

b. The Oxides of Potassium. Potassium oxide, K_2O , can be produced by heating potassium nitrite or nitrate with potassium in the absence of air. If

potassium metal is burned in a calculated amount of air, potassium peroxide, K_2O_2 , will be formed. Potassium metal will react at room temperature with oxygen to form potassium tetroxide, K_2O_4 . Potassium tetroxide, an orange-red solid, will decompose on heating to form oxygen and the peroxide, K_2O_2 . All of the potassium oxide compounds react vigorously with water to yield KOH, oxygen, and hydrogen peroxide.

c. Potassium Hydroxide, KOH. Potassium hydroxide can be prepared either by the electrolysis of potassium chloride, KCl, or by reacting calcium hydroxide with potassium carbonate, K_2CO_3 . KOH is highly deliquescent and very soluble in water. Its chemical behavior is similar to that of sodium hydroxide, NaOH. Its solutions are strongly basic.

d. The Nitrogen Compounds. Potassium, like sodium, can react with nitrogen in an electric discharge tube to form potassium nitride, K_3N . K_3N is green-black in color, and it is rapidly attacked by water to form KOH and NH_3 . Potassium azide, KN_3 , can also be formed by the action of nitrogen upon potassium. KN_3 will decompose upon heating in a vacuum to form K_3N and nitrogen gas.

Potassium nitrate, KNO_3 , is made by reacting $NaNO_3$ with KCl. KNO_3 is more soluble in hot water than in cold. It will melt at 334° and be decomposed. When heated at temperatures above 400° , KNO_3 will lose oxygen to form potassium nitrite, KNO_2 . Potassium nitrite will decompose at 850° to produce potassium peroxide, K_2O_2 . It is soluble in water, and when the solution is boiled it will hydrolyze to produce nitrous acid, HNO_2 .

e. The Sulfide, Sulfate, and Sulfite Compounds. Potassium will react with sulfur to form potassium monosulfide, K_2S , and potassium polysulfide, K_2S_2 . The monosulfide compound, K_2S , is a colorless crystalline compound that is hygroscopic and will react rapidly with water.

Potassium sulfate, K_2SO_4 , like sodium sulfate, occurs freely in nature. It is prepared by extracting the mineral deposit, schonite, $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$, and treating the concentrated aqueous solution with potassium chloride. K_2SO_4 is very soluble in water. If K_2SO_4 is treated with the proper quantity of sulfuric acid and the mixture heated, potassium hydrogen sulfate, or potassium bisulfate, $KHSO_4$, is produced. $KHSO_4$ dissolves in water to give

Table II. Solubility of Potassium Compounds

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Bromides	KBrO ₃	3.1° 13.3 ⁴⁰	49.75 ¹⁰⁰	Slightly soluble in alcohol; insoluble in acetone
	KBr	53.48°	102 ¹⁰⁰	0.5 alcohol; soluble in glycerin; slightly soluble in ether
	KAuBr ₄	Slightly soluble		Soluble in alcohol
	KIBr ₂	Decomposes		
Chlorides	K ₂ PtBr ₆	Very soluble	Very soluble	
	KClO ₃	7.1 ²⁰	57 ¹⁰⁰	0.83 alcohol; soluble in alkali
	KClO ₄	0.75°	21.8 ¹⁰⁰	Insoluble in alcohol and ether
	KCl	34.7 ²⁰	56.7 ¹⁰⁰	Slightly soluble in alcohol; soluble in alkali, ether and glycerin
Oxides	KClO	Very soluble	Very soluble	
	K ₂ Ru(H ₂ O)Cl ₅	Soluble	Soluble	Slightly soluble in alcohol
	K ₂ Ru(OH)Cl ₅	Soluble; decomposes	Soluble	Insoluble in alcohol
	KAuCl ₄	61.8 ²⁰	80.2 ⁶⁰	Soluble in acid; 25 alcohol
Fluorides	KCrO ₃ Cl	Soluble; decomposes		Soluble in acid
	KICl ₄	Decomposes		Decomposes in ether
	KF	92.3 ¹⁸	Very soluble	Soluble HF and NH ₃ ; insoluble in alcohol

(Table continues on following page.)

Table II. Solubility of Potassium Compounds (Continued)

<u>Compound</u>	<u>Formula</u>	<u>Water Solubility</u>		<u>Other Solvents</u>
		<u>Cold</u>	<u>Hot</u>	
	KF · 2H ₂ O	349.3 ¹⁸	Very soluble	Soluble in HF; insoluble in alcohol
	KHF ₂	41 ²¹	Very soluble	Soluble in KC ₂ H ₃ O ₂ ; insoluble in alcohol
	K ₂ SiF ₆	0.12 ^{17.5}	0.954 ¹⁰⁰	Soluble in HCl; insoluble in NH ₃ and alcohol
	K ₂ TaF ₇	Slightly soluble; decomposes		Slightly soluble in HF
	K ₂ ThF ₆ · 4H ₂ O	2.15	6.6	Decomposes in acid; insoluble in alcohol
	K ₂ TiF ₆ · H ₂ O	.556 ⁰ 1.320	1.27 ²¹	Min. acid; insoluble in NH ₃
	K ₂ ZrF ₆	.781 ²	25 ¹⁰⁰	Insoluble in NH ₃
Iodides	KIO ₃	4.74 ⁰	32.3 ¹⁰⁰	Soluble in KI; insoluble in alcohol and NH ₃
	KIO ₄	0.66 ¹³	Soluble	Very slightly soluble in KOH
	KI	127.5 ⁰	208 ¹⁰⁰	14.3 alcohol; soluble in NH ₃ ; slightly soluble in ether
	KI ₃	Very soluble		Soluble in alcohol and KI
	KAuI ₄	Soluble; decomposes		Soluble in dilute solution KI

	K_3IrI_6	Very soluble		Insoluble in alcohol
	KH_9I_3	Decomposes		Soluble in alcohol, ether, KI and acetic acid.
	K_2PtI_6	Soluble	Soluble; decomposes	Insoluble in alcohol
Nitrides	K_3N	Decomposes		
	KNO_3	Soluble	Soluble	Very soluble in NH_3 and alcohol; soluble in alcohol; insoluble in 94% alcohol
	$K_2Pt(NO_2)_4$	Soluble	Soluble	
	KNO_2	Soluble	Soluble	Soluble in alcohol
Oxides	K_2O	Very soluble	Very soluble	Soluble in alcohol and ether
	K_2O_2	Very soluble	Very soluble	
	K_2O_4	Very soluble; decomposes	Very soluble	Decomposes in alcohol
Sulfides	K_2S	Soluble	Very soluble	Soluble in glycerin; insoluble in ether
	KHS	Decomposes	Decomposes	Soluble in alcohol
	K_2S_2	Soluble	Decomposes	Soluble in alcohol
Sulfate	K_2SO_4	Soluble	Soluble	
	$KHSO_4$	Soluble	Soluble	

an acidic solution, and it can be used to convert oxides and silicates into sulfates. When it is heated at a temperature of 200° , it is converted into potassium pyrosulfate, $K_2S_2O_7$. When $K_2S_2O_7$ is strongly ignited, SO_3 is released and normal potassium sulfate, K_2SO_4 , is produced. The electrolysis of a concentrated solution of $KHSO_4$ will produce potassium peroxydisulfate, $K_2S_2O_8$.

Potassium hydrogen sulfite, or potassium disulfite, $KHSO_3$, can be produced by saturating a solution of potassium carbonate or potassium hydroxide with sulfur dioxide. Normal potassium sulfite, K_2SO_3 , is formed by treating the solution with an additional amount of potassium carbonate. The sulfites are easily decomposed by heating to form stable sulfate, K_2SO_4 . The sulfites can also be easily oxidized to produce the corresponding sulfates.

f. The Halogen Compounds of Potassium. Potassium fluoride, KF , is obtained by neutralizing hydrofluoric acid with KOH or K_2SO_3 . If the solution is evaporated, a white deliquescent solid is obtained. If the solution is treated with an equimolecular amount of hydrofluoric acid, potassium hydrogen fluoride, KHF_2 , is produced.

Potassium chloride, KCl , can be obtained in the natural state; however, it is frequently produced by the action of HCl upon potassium hydroxide. If a hot solution is treated with bromine, or iodine, respectively, potassium bromide, KBr , and potassium iodide, KI , are produced. All of the potassium halide salts are completely ionized and are readily soluble in water at room temperature.

Potassium chlorate, $KClO_3$, potassium perchlorate, $KClO_4$, potassium hypochlorite, $KClO$, potassium bromate, $KBrO_3$, and potassium iodate, KIO_3 , are all salts of the oxygen acids of the halogens. $KClO_3$ is prepared by passing chlorine gas into hot, concentrated potassium hydroxide. It is a colorless salt that is much more soluble in hot water than in cold. $KClO_3$ can also be prepared by adding hot KCl to hot $NaClO_3$ solution. $KClO_3$ is a strong oxidizing agent, and it will decompose with a violent explosion to produce free chlorine and oxygen. $KBrO_3$ and KIO_3 can be produced in the same manner as $KClO_3$, and they exhibit the same chemical reactions as $KClO_3$ does. Potassium perchlorate, $KClO_4$, is produced by an anodic oxidation of $KClO_3$. It is produced as a colorless compound that is used as a strong oxidizing

agent. Potassium hypochlorite, $KClO \cdot 6H_2O$, is produced either by the reaction of chlorine gas upon a cold solution of KOH or by an electrolysis of KCl solutions in the presence of potassium hydroxide and chlorine. Potassium hypochlorite can be easily reduced to chloride ions and oxygen.

g. The Phosphate Compounds of Potassium. Potassium hydroxide, like sodium hydroxide, can also enter into reaction with H_3PO_4 to form potassium dihydrogen phosphate, KH_2PO_4 , potassium monohydrogen phosphate, K_2HPO_4 , and tripotassium phosphate, K_3PO_4 . Aqueous solutions of KH_2PO_4 are acidic, while solutions of K_2HPO_4 and K_3PO_4 vary in their alkalinity. If KH_2PO_4 is heated, a series of potassium metaphosphates, KPO_3 , are formed. When K_2HPO_4 is treated, it will decompose to form $K_4P_2O_7$ and water. K_3PO_4 is stable toward heat.

h. The Carbonate Compounds. Potassium carbonate, K_2CO_3 , is prepared by a series of chemical reactions involving magnesium carbonate and potassium chloride. Potassium hydrogen carbonate, $KHCO_3$, is produced either by passing carbon dioxide gas into a saturated solution of K_2CO_3 or by passing carbon dioxide over a mixture of K_2SO_3 and charcoal. K_2CO_3 and $KHCO_3$ solutions are alkaline because of the basic action of the CO_3^{2-} ions and the slight hydrolysis of the HCO_3^- ions.

i. The Cyanides and Cyanate Compounds. Potassium forms complex cyanides with iron: i.e., potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$. Potassium ferrocyanide is prepared as a by-product of the coal gas industry. In the process, hydrogen cyanide, HCN, is released from the coal gas to react with FeO to form ferrocyanic acid, $H_4Fe(CN)_6$, which reacts with Fe_2O_3 to produce $Fe_4[Fe(CN)_6]_3$. This compound is roasted with lime to give a soluble calcium ferrocyanide. The solution is then heated with potassium chloride to form lemon-yellow crystals of the hydrate, $K_4Fe(CN)_6 \cdot 3H_2O$. The potassium ferrocyanide can be solubilized in acid and converted to potassium ferricyanide, $K_3Fe(CN)_6$, by oxidizing the solution with chlorine. When ferrous ions, Fe^{+2} , react with potassium ferricyanide, the ferricyanide ions are reduced to ferrocyanide ions and a soluble compound of potassium berlinate, $KFe[Fe(CN)_6]_3$, or Prussian blue is formed.

Potassium cyanide, KCN , is formed by heating potassium ferrocyanide with K_2CO_3 in the presence of iron. It can also be made by passing nitrogen or ammonia over a mixture of fused K_2CO_3 and carbon. KCN can be quickly changed into potassium cyanate, $KOCN$, by mixing PbO with the fused cyanide. KCN can enter into a reaction with sulfur to produce potassium thiocyanate, $KSCN$. Potassium thiocyanate can also be prepared by treating the cyanide with ammonium polysulfide or sodium thiosulfate.

j. Other Potassium Compounds. The roasting of manganese dioxide with KOH in air will produce potassium manganate, K_2MnO_4 , which in turn can react with H_2SO_4 or chlorine water to form potassium permanganate, $KMnO_4$. $KMnO_4$ is a purple-black solid that dissolves readily in water. Its solutions are strong oxidizing agents in both acid and alkaline conditions. When it is heated above 200° , it will lose oxygen to yield MnO_2 and K_2MnO_4 .

Potassium chloride, KCl , will react with chloroplatinic acid, H_2PtCl_6 to produce potassium chloroplatinate, K_2PtCl_6 . This alkali chloroplatinate is a yellow salt that is very insoluble in water. The water insoluble salt, potassium cobaltinitrite, $K_3[Co(NO_2)_6] \cdot 3H_2O$, is formed by adding a large excess of potassium nitrite to an acetic acid solution of sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$. Potassium can also enter into reactions with tartaric acid, chlorate ions, and picric acid, respectively, to produce insoluble salts, such as potassium hydrogen tartrate, $KHC_4H_4O_6$, potassium perchlorate, $KClO_4$, and potassium picrate, $KOC_6H_2(NO_2)_3$.

B. The Analytical Chemistry of Potassium

Potassium, after its isolation and separation from other elements, is most often determined gravimetrically as potassium chloroplatinate, K_2PtCl_6 , (3-6) or potassium perchlorate, $KClO_4$. (7-11) Potassium can also be precipitated as the double cobaltinitrite of potassium and sodium, $K_2Na[Co(NO_2)_6]$. (12-19) However, the composition of the precipitate varies with the ionic composition of the solution. Potassium has also been determined gravimetrically by being precipitated as potassium sulfate, K_2SO_4 ; (20) potassium molybdatephosphate, $K_3(MoO_3)_2$; (21) potassium periodate, KIO_4 ; (22-26) potassium hexanitritocuprate, $K_2PbCu(NO_2)_6$; (27) potassium perrhenate, $KReO_4$; (28) potassium hydrogen tartrate, $CO_2H \cdot (CHOH)_2CO_2K$; (29)

potassium 6-chloro-5-nitrotoluene-m-sulfonate, $\text{CH}_3\cdot\text{C}_6\text{H}_2(\text{Cl})(\text{NO}_2)\cdot\text{SO}_3\text{K}$; (30)
potassium diliturate, $\text{C}_4\text{H}_2\text{O}_5\text{N}_3\text{K}$; (31) potassium dipicrylaminate, $\text{C}_{12}\text{H}_4\text{O}_{12}\text{N}_7\text{K}$; (32,33)
potassium fluoborate, KBF_4 ; (34) or potassium tetraphenylborate, K_2TPB . (35-41)

Most of these compounds are satisfactory gravimetric forms⁽²⁸⁾ for determining potassium and can be used in the radiochemical analysis of sample materials for the radioactive potassium isotopes.

The isolation and separation of potassium from other elements has most frequently been completed by precipitation methods. More recently, solvent extraction and chromatography methods have been employed. These separation methods can generally be described as follows:

1. Separations By Precipitation. Potassium and the other alkali elements (sodium, lithium, rubidium, and cesium) can be best separated from other elements by methods first suggested by Berzelius⁽⁴²⁾ and Smith.⁽⁴³⁾ Especially adapted to the decomposition of minerals, the Berzelius method⁽⁴²⁾ and its modifications⁽⁴⁴⁻⁴⁶⁾ uses mixtures of $\text{HF-HClO}_4\text{-H}_2\text{SO}_4$ to decompose the materials and then converts the alkali sulfates to chlorides for the final precipitation of the potassium as either the chloroplatinate⁽³⁻⁶⁾ or perchlorate.⁽⁷⁻¹¹⁾ Smith's method⁽⁴³⁾ and its modifications⁽⁴⁶⁻⁴⁸⁾ decomposes the potassium-bearing material (usually a mineral) 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 is 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 alkali metals are treated either with HClO_4 or H_2PtCl_6 to precipitate the potassium either as KClO_4 ⁽⁷⁻¹¹⁾ or as K_2PtCl_6 .⁽³⁻⁶⁾

Barium, strontium, magnesium, borates, sulfates, and phosphates can interfere in either of these methods for the determination of potassium and the other alkali metals. The removal of calcium by an ammonium carbonate and oxalate precipitation also removes barium and strontium;⁽⁴⁹⁾ magnesium can be separated either by a precipitation of magnesium ammonium phosphate⁽⁵⁰⁾

or magnesium oxinate.⁽⁵¹⁾ Borates can be removed as volatile methyl borates by adding methyl alcohol to the hydrochloric acid solution and evaporating the mixture to dryness.⁽⁴⁹⁾ The addition of barium chloride solution to the chloride mixture will precipitate the sulfate ions as BaSO_4 ;⁽⁴⁹⁾ the excess barium can be removed by a precipitation with ammonium carbonate.⁽⁴⁹⁾ Phosphates can be removed from the alkali chloride solution by a precipitation either with zinc carbonate⁽⁵²⁾ or with an FeCl_3 solution at a controlled pH.⁽⁴⁹⁾

Potassium may be separated from sodium and lithium by several precipitation methods. The most important ones are based upon the formation of the alkali chloroplatinates⁽³⁻⁶⁾ or the perchlorates.⁽⁷⁻¹¹⁾ 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 K_2PtCl_6 . However, several extractions of the chloroplatinate salts may be necessary to remove all of the lithium. Besides the direct precipitation with chloroplatinic acid, H_2PtCl_6 , a solution of lithium chloroplatinate can be used as the precipitating agent.⁽⁵³⁾ Rubidium and cesium also form insoluble chloroplatinates. If the chloroplatinate are precipitated from a nitrate solution with H_2PtCl_6 , potassium (and Rb and Cs) can be separated from large amounts of sodium, iron, aluminum, manganese, and other salts.⁽⁵⁾ If the precipitation is made from a chloride solution, an immediate and quantitative separation of potassium (and Rb and Cs) from the same elements can be obtained by dissolving the chloroplatinates in 60-70% alcohol and a few drops of ethyl ether.⁽⁵⁾ In the perchlorate method, 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 KClO_4 . The perchlorate salts of Cs^{+1} , Rb^{+1} , NH_4^{+1} , and Tl^{+1} are also insoluble and will interfere. Sulfate ions must also 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.

Potassium can be separated from sodium, lithium, and many other elements by the trisodium cobaltinitrite method.⁽¹²⁻¹⁹⁾ NH_4^{+1} , Cs^{+1} , Rb^{+1} , V^{+4} , U^{+6} , Sb^{+3} , Bi^{+3} , and Sn^{+4} interfere in this method. Large amounts of sodium can

be separated by saturating an acid solution with gaseous hydrochloric acid.⁽⁴⁹⁾

Acetone readily dissolves lithium chloride so that it can be dissolved and separated from insoluble potassium chloride.⁽⁵⁴⁾ Sodium, barium, and strontium chlorides are also insoluble and would interfere in this method. Rubidium and cesium can be separated from potassium by precipitating them from a dilute HNO_3 solution with 9-phosphomolybdic acid.^(5,55) Potassium is soluble in this system and is recovered by a chloroplatinate precipitation.⁽⁵⁾ Potassium, rubidium, and cesium can be separated from sodium and lithium by a chloroplatinic acid precipitation,⁽³⁻⁶⁾ converted to the chlorides and the potassium separated from rubidium and cesium by extracting the chloride mixture with absolute alcohol^(56,57) saturated with hydrochloric acid gas. The rubidium and cesium chlorides are insoluble in this mixture. This method is a rather long and tedious one; it is sometimes necessary to re-extract the chlorides in order to remove all of the KCl , and depending upon the concentrations of all three elements, each element can interfere in the determination of the others.

Potassium (and ammonium ions) can be separated from sodium, lithium, and magnesium by a sodium tetraphenylboron precipitation.⁽³⁵⁻⁴¹⁾ The insolubility of potassium tetraphenylboron suggests that this is an excellent gravimetric form for the determination of potassium. In one of these studies,⁽³⁸⁾ it was found that the ammonium ion interference could be minimized by operations involving fuming with HNO_3 , volatilization of ammonia by heating with sodium hydroxide and a hypobromite oxidation of the remaining traces of ammonium salts.

2. Separation By Electrolysis. 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.⁽⁵⁸⁾ 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.

3. Solvent Extraction Separations. The polyiodides of the alkali metals can be extracted with nitromethane.⁽⁵⁹⁾ Their distribution ratios increase in the order $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ and are dependent upon the amount

of free iodine added to the system. The use of 80% ethyl alcohol^(3-6, 53) 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% HClO₄ mixtures in separating the alkali perchlorates⁽⁷⁻¹¹⁾ has already been discussed. The acetone extraction⁽⁵⁴⁾ of soluble LiCl from insoluble KCl has also been mentioned above.

4. Chromatographic Separations

a. With Inorganic Absorbents. A chromatographic ion exchange system involving an alumina column has been used to separate fluoride and sulfate ions from potassium before its determination as KClO₄.⁽⁶⁰⁾ The column was treated with 1 M HClO₄ until the effluent showed an acid reaction. Then the water extracts of decomposed silicates were passed through the column and the potassium recovered from the effluent.

b. With Organic Absorbents. Chromatographic columns of violuric acid, mixed with barium sulfate, diatomaceous earth or starch, have been used to separate potassium chloride from sodium and magnesium chlorides.⁽⁶¹⁾

Potassium has also been separated from sodium by use of a violuric acid column⁽⁶²⁾ and by use of a column of 5-oxo-5-oximino-3-phenyloxazoline.⁽⁶³⁾

c. With Ion Exchange Resins. Mixtures of K, Na, Rb, and Cs chlorides have been separated by adsorbing the mixture on Dowex-50 and using either 0.15 N HCl⁽⁶⁴⁾ or 0.7 N HCl⁽⁶⁵⁾ as the elutriants. Potassium has been completely separated from Na, Rb, and Cs by adsorbing a mixture of the chlorides on an Amberlite IR-100 or IR-1 resin column and eluting with HCl solutions.^(66,67) Potassium and sodium were eluted with 0.1 N HCl and the rubidium and cesium were eluted with 1 N HCl. Amberlite IR-100 resin and HCl have also been used to separate milligram amounts of KCl from milligram amounts of NaCl.⁽⁶⁸⁾ Milligram amounts of KCl containing less than 0.1 ppb of Cs and 1.0 ppb of Rb have also been prepared by use of a cation resin column.^(69,70) Potassium and sodium have been separated from each other by use of a column of Wofatit KS ion exchange resin and 0.1 N HCl as the elutriant.⁽⁷¹⁾ Cation ion exchange resins have also been used to separate K and Na from each other and from Mg and Cs in milk ash,⁽⁷²⁾ K from Na in blood,⁽⁷³⁾ K from insoluble silicates,⁽⁷⁴⁾ and K and Na from lithium.⁽⁷⁵⁾

The alkali metal complexes of uramildiacetic acid were studied by use of a cationic resin.⁽⁷⁶⁾ Lithium and sodium form stable complexes but potassium does not. The complexes were separated by use of a sulfonic acid resin, pretreated with either dimethyl amine or tetramethylammonium hydroxide, and elutions with alkaline solutions. Lithium and sodium, but not potassium, rubidium, or cesium, form complexes with the chelating agent, ethylenediaminetetraacetic acid, EDTA, and can be separated from K, Rb, and Cs, and from each other by eluting an anion resin column of Dowex-1 (4% crosslinkage) with 0.13 M EDTA solution.⁽⁷⁷⁾

d. By Paper Chromatography. Tracer quantities of radioactive K⁴² (12.4 h) have been separated from Na²⁴ (15 h) by use of paper chromatography and a solvent mixture of conc. HCl-water-0.05% tartaric acid (1:10:4).⁽⁷⁸⁾ In other chromatographic studies with paper columns, the movement rate of potassium ions has been studied using solvents such as dipicrylamine in a solution of Na₂CO₃,⁽⁷⁹⁾ quercitin in acid and alkaline media,⁽⁸⁰⁾ and complex forming mixtures, e. g., butanol-HNO₃-acetylacetone,⁽⁸¹⁾ alcohols in HCl,^(82,83) butanol in HCl,⁽⁸³⁾ alcohols in HNO₃,⁽⁸⁴⁾ ketones in HCl,⁽⁸⁵⁾ butanol-HBr,⁽⁸⁶⁾ phenol,⁽⁸⁴⁾ or collidine in HNO₃.⁽⁸⁷⁾

KCl has been quantitatively separated from Li and Na chlorides using methanol as a solvent,^(88,89) ethanol in water,⁽⁸⁹⁾ acetone in water,⁽⁸⁹⁾ methyl ethyl ketone in methanol,⁽⁹⁰⁾ and with acetone-, ethanol-, butanol-, and pentanol-methanol mixtures.⁽⁹⁰⁾ The alkali acetates can also be separated by paper chromatography using ethanol-2N acetic acid as a solvent.⁽⁹¹⁾ The same system was used later to quantitatively determine K in a alkali mixture.⁽⁹²⁾ Potassium has been separated from Na, Mg, and Ca in biological samples by the same solvent mixture.⁽⁹³⁻⁹⁶⁾ Propanol-methanol mixtures as solvents have been used to separate K from Na, NH₄, Mg, and Li⁽⁹⁷⁾ and from Na, Mg, and Ca.⁽⁹⁸⁾ These solvents have also been used to separated alkali hydroxides, citrates, and sulphates.⁽⁹⁹⁻¹⁰¹⁾

K has been separated from rubidium and cesium by using conc. HCl-methanol-n-butanol-isobutylmethyl ketone as a solvent⁽¹⁰²⁾ and by phenol saturated with 2 N HCl.⁽¹⁰³⁾ Potassium in urine has been determined also by a paper chromatographic technique.⁽¹⁰⁴⁾

An electrolytic method of detecting the alkali metals by placing the paper sprayed with phenolphthalein between two graphite electrodes at a voltage of 6 volt for 5 seconds has also been used to separate the alkali metals. (105)

IV. DISSOLUTION OF SAMPLES CONTAINING POTASSIUM

Most of the analytical methods used in determining potassium and the other alkali metals require that they be collected as the chlorides. Most of the simple potassium salts are readily soluble in water or dilute acid, and most metals and alloys containing potassium can be put into solution with volatile acids such as HCl, HNO₃, 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, the material can be solubilized by either the Berzelius method⁽⁴²⁾ or the Smith method.⁽⁴³⁾ These methods are most frequently used on silicate rocks. The Berzelius method attacks the rock with HF and H₂SO₄, then expels the excess fluorine and silicon 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, the decomposition is accomplished by heating the powdered rock 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.

Typical methods involving the decomposition of soils include treatments with ammonium acetate, HCl, and aqua regia,^(106,107) and leachings with either HNO₃,⁽¹⁰⁸⁾ HCl-HF,⁽¹⁰⁹⁾ and H₂SO₄.⁽¹¹⁰⁾ Biological materials, such as tissues, body fluids, vegetation, etc., can be decomposed with HCl, HNO₃, HNO₃-H₂SO₄, or HNO₃-HClO₄ mixtures.^(106,107)

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

V. SAFETY PRACTICES

The decomposition and processing of any material by a chemical means inherently can be hazardous. Some of the inactive potassium compounds are extremely toxic and should be handled carefully. Likewise, some of the reagents used in an analysis can be harmful. Thus, adequate safety precautions should be followed in processing any sample material. Pieters and Creyghton⁽¹¹¹⁾ have recently issued a manual on safe laboratory practices. This manual, as well as others on laboratory safety, should be consulted before any analysis is undertaken.

The processing of 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 wide spread contamination can result. Information on safe handling practices for radioactive materials appear in such sources as the Oak Ridge National Laboratory's Master Analytical Manual⁽¹¹²⁾ and in the International Atomic Energy Agency's publication, entitled, "Safe-Handling of Radioisotopes."⁽¹¹³⁾ Many other similar sources of information exist and should be consulted.

VI. COUNTING TECHNIQUES FOR THE RADIOACTIVE POTASSIUM ISOTOPES

The nuclear characteristics of the radioactive isotopes of potassium are summarized in Table I of this monograph. Potassium is unique in that one of its stable isotopes, K⁴⁰, is a natural radioactive source having a half-life of 1.39×10^9 years. This natural potassium radioactivity can sometimes be used in measuring the potassium content of a sample material. For example, the potassium content of iron meteorites was measured by isolating the potassium and then measuring the K⁴⁰ by means of a low-level beta counter.⁽¹¹⁴⁾ The assay of the potassium content of rocks and minerals has also been accomplished by isolating K⁴⁰ and measuring its radioactivity.⁽¹¹⁵⁾

The other most frequently used potassium radioisotope is K⁴² (12.4 h). Its radioactivity can be measured by such counting techniques as Geiger-Mueller counting, proportional counting, or gamma scintillation spectrometry.⁽¹¹⁶⁻¹¹⁹⁾ Generally, the sample material containing K⁴² must be processed radiochemically

before the radioactivity measurements are made. However, it has been possible to determine small amounts of potassium in silicon metal by a non-destructive radioactivation analysis involving gamma scintillation spectrometry⁽¹²⁰⁾ to measure the radioactivity of K⁴². Potassium-42 has also been determined in biological materials by nondestructive radioactivation analysis methods.⁽¹²¹⁻¹²⁶⁾

VII. RADIOCHEMICAL PROCEDURES FOR THE POTASSIUM RADIONUCLIDES

The analytical procedures used in radiochemistry are 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 separate and to determine the amount of radioactivity of a particular radioelement in a radionuclide mixture, or (3) to complete a radioactivation analysis.

In order to accomplish any one of the above interests, radiochemistry usually considers the isolation of the desired radionuclide by either carrier or carrier-free separation methods. Carrier methods are most frequently used 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 a carrier-free separation, 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 radioactivity measurements. Usually a carrier-free method is used to obtain a radionuclide for an absolute measurement of its radioactivity.

Analytical radiochemistry uses separation methods involving precipitation, solvent extraction, chromatography, volatilization, and electrolysis to isolate a radioelement in a suitable form for a measurement of its radioactivity. Carrier radiochemistry is unique in that it is not always necessary to recover completely the added amount of carrier 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.

Both carrier-free and carrier radiochemical analysis procedures exist for the potassium radionuclides. Such procedures as these have evolved from each investigator's choice of ideas and techniques similar to those reported in Section III of this monograph. Most of these procedures have been originated to separate the potassium radionuclides for use as radioactive tracers, (127) and to determine stable potassium by radioactivation analysis methods. (128,129)

A carrier-free method has been used in the radioactivation analysis determination of trace potassium in alkali carbonates and chlorides. (66,130) The paper chromatography method cited earlier⁽⁷⁸⁾ is also a carrier-free method. Almost all of the chromatographic separations mentioned earlier could be used in carrier-free separations of radiopotassium.

Carrier methods are now employed in the preparation and production of radioactive tracers of potassium (127) and in radioactivation analysis. (128,129) In radioactivation analysis, trace amounts of potassium have been determined in water, (131) magnesium, (132) and minerals. (133) Samples of meteorites (134) and tungsten metals (135) have been analyzed in the same manner. Aluminum, stainless steel, soils, vegetation, ore concentrates, clays, sand, limestone, cement, tissue, resins, lithium carbonate, and lithium iodide have also been analyzed for stable potassium content by a neutron radioactivation analysis. The separation methods are described in Procedure 7 that follows. (136,137)

In each of the procedures included in this section, information is given about the specific use of the procedure, the type of material analyzed, the type of nuclear bombardment, etc. Whenever possible, a statement is made about the decontamination levels achieved by the particular procedure cited.

PROCEDURE 1

Procedure Used In: Preparation of radioactive tracers

Method: Precipitation

Element Separated: Potassium radionuclides

Type Material Bombarded: Lithium Chloride

Type of Nuclear Bombardment: 20-60 Mev alphas

Procedure By: Brooks (Reported by Meinke⁽¹²⁷⁾)

Separation Time: 1 hour

Chemical Yield of Carrier: Quantitative

Decontamination: Radiochemically purity possible

Equipment Required: Standard

Procedure:

1. Dissolve LiCl in about 3 cc water; add KCl carrier (~ 20 mg).
2. Add ~ 5 cc of 72% HClO₄ and cool in ice.
3. Centrifuge.
4. The KClO₄ may be recrystallized as many times as desired by heating it to ~ 90° C with 1 cc of 72% HClO₄ and then cooling in ice.

Remarks:

4 recrystallizations can be made in 1 hour of chemistry. About 1/2% is lost per recrystallization by doing it this fast. A trace of P³² sometimes was not removed by this chemistry.

NH₄⁺ salts interfere. Separation from Na is good. No Rb or Cs contamination was found.

PROCEDURE 2

Procedure Used In: Preparation of radioactive tracers

Method: Precipitation

Element Separated: Potassium radionuclides

Type Material Bombarded: Lithium chloride

Type of Nuclear Bombardment: 20-60 Mev alphas

Procedure By: Brooks (Reported by Meinke⁽¹²⁷⁾)

PROCEDURE 2 (Continued)

Separation Time: 40 minutes or less

Chemical Yield of Carrier: 50% or more

Decontamination: Radiochemically purity possible

Equipment Needed: Standard

Procedure:

1. Dissolve LiCl in ~ 5 cc of H₂O.
2. Add 10 cc of Naphthol-yellow-S (5% solution) cool and centrifuge.
3. Recrystallize from about 5 cc of 5% NY8.
4. The ppt can be dissolved quickly in water or weak acid.
5. Scavenge with Fe(OH)₃.

Remarks:

NH₄⁺ salts interfere.

PROCEDURE 3

Procedure Used In: Radioactivation analysis

Method: Ion Exchange (carrier-free separation)

Element Separated: K⁴² (12.4 h)

Type Material Analyzed: Alkali carbonates and chlorides^(66,130)

Type Nuclear Bombardment: K⁴¹(n,γ)K⁴²

Procedure By: Brooksbank and Laddicotte⁽⁶⁶⁾ (Reported in detail by Laddicotte⁽¹³⁰⁾)

Separation Time: Several hours

Chemical Yield of Carrier: A carrier-free separation

Decontamination: Excellent from radionuclides of Na, Rb, 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/cm² for 16 hours or longer (Note 3).

PROCEDURE 3 (Continued)

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 below.

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 Potassium

1. Connect the ion-exchange column to a reservoir (Note 7) 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 1 ml per minute.
2. Continue the flow of the 0.1 M HCl through the column and collect and

PROCEDURE 3 (Continued)

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. Allow the flow of the eluate to continue until an additional 700 ml has been collected in a second collection vessel (or series of beakers). Process this fraction of the eluate as instructed in Step 1 of Part D below.
5. If rubidium and cesium are not to be determined, stop the flow of eluate from the column after this collection (Note 10).

D. Preparation of K⁴² Eluate For Radioactivity Assay

1. Evaporate to dryness the solution that was collected in Step 4 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 H₂O, transfer the rinsings to the flask, and dilute the solution to volume.
- Assay the solution for K⁴² radioactivity as instructed in Part E below.

E. Measurement of K⁴² Radioactivity and Calculation of Stable Potassium Content of Test Sample

1. The K⁴² 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 11).
2. Following the radioactivity measurements, correct the observed K⁴² radioactivity for decay (Note 12), 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 potassium in the test sample:

$$\% \text{ K in Test Sample} = \frac{\text{Corrected K}^{42} \text{ radioactivity in Test Sample}}{\text{Corrected K}^{42} \text{ radioactivity in Comparator Sample}} \times 100$$

Notes:

1. Use at least 0.1-0.2 gram portions.
2. Use from 0.025 to 0.030 gram of potassium carbonate.
3. The limits of measurement for this procedure is about 0.05 micrograms of potassium.

PROCEDURE 3 (Continued)

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} which is 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. If Rb and Cs are to be determined, continue as follows: (a) collect the next 800 ml and process for Rb; (b) then, strip the column with at least 1 N HCl and process this fraction for Cs. Rubidium and cesium comparator samples should have been irradiated, if stable Rb and Cs are to be determined in a sample.
11. Gamma-ray energy discrimination may be used here.
12. Decay measurements may be followed, if required.

PROCEDURE 4

Procedure Used In: Radioactivation analysis

Method: Precipitation

Element Separated: K⁴² (12.4 h)

Type Material Bombarded: Water

Type of Nuclear Bombardment: K⁴²(n,γ)K⁴²

Procedure By: Blanchard, Leddicotte, and Moeller (131)

Separation Time: Not estimated by the authors

Chemical Yield of Carrier: 60-70%

Equipment Needed: Standard

Procedure:

1. 30 mls of water was placed in a polyethylene bottle and irradiated for 16 hours in a flux of 6.5×10^{11} n/cm²/sec.

2. If any specific element, such as potassium, is to be analyzed quantitatively, a known amount of K₂CO₃ 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 potassium is found in the last step (Part II of the "Scheme") with the Soluble Group along with sodium and rubidium. Because of the high energy of Na²⁴, 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, in which the potassium and rubidium perchlorates are insoluble.

5. The radioactivity of each of these groups including the potassium as K⁴² (12.4 h) was analyzed by gamma scintillation spectrometry; K⁴² decays with gamma radiations of 1.51 Mev.

6. Following the radioactivity measurements, correct the observed K⁴² 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 stable potassium in the water sample:

$$\% \text{ K in H}_2\text{O Sample} = \frac{\text{Corrected K}^{42} \text{ radioactivity in H}_2\text{O sample}}{\text{Corrected K}^{42} \text{ radioactivity in standard sample}} \times 100$$

Chemical Separation Scheme

- 1) Add the radioactive sample to a 50 milliliter centrifuge tube. Aerate to remove radioactive gases. Acidify with HNO₃ 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 H₂S. Centrifuge.
-
- 4) Precipitate: CuS + As₂S₃. 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 HNO₃. Cool solution and make 1:1 with conc. HCl. Neutralize with conc. NH₄OH 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 H₂S. 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 H₂S. Add (NH₄)₂H(PO₄) and an excess of NH₄OH. Digest. Centrifuge.
-
- 10) Precipitate: Ce, Ba, and Sr phosphates. Wash, filter, mount, and count. Designate as the SOLUBLE GROUP.
- 11) Supernate: Ce, Ba, and Soluble ions. Designate as the ALKALINE GROUP.

PROCEDURE 5

Procedure Used In: Radioactivation analysis

Method: Precipitation

Element Separated: K⁴² (12.4 h)

Type Material Bombarded: Magnesium

Type Nuclear Bombardment: K⁴¹(n, γ)K⁴²

Procedure By: Atchison and Beamer⁽¹³²⁾

Separation Time: Approximately 3 hours

Chemical Yield of Carrier: Possible quantitative

Equipment Needed: Standard

Procedure:

A. Irradiation of Sample Material

1. Magnesium turnings were irradiated for 4 weeks at the Oak Ridge National Laboratory in a flux of 5×10^{11} n/sec/cm² along with a weighed portion of K₂CO₃ for a standard (Note 1).

B. Radiochemical Separation of K⁴²

1. After the irradiation, dissolve a weighed portion of the Mg sample in 16 ml of 12 M HCl in the presence of 60 mg of K and 80 mg of Na carrier and 10 ml of water in a 250 ml beaker.
2. Evaporate the contents to a small volume to remove excess acid.
3. Transfer the solution to a 100-ml mixing cylinder and dilute to approximately 75 ml and add 13 ml of n-butylamine. Dilute to 100 ml and mix well.
4. Centrifuge the slurry and decant the clear liquid through a dry filter paper. Place a 60-ml aliquot in a 150 ml beaker and evaporate to dryness on a hot plate. Sublime the amine hydrochloride away using a Bunsen flame while passing a stream of nitrogen into the beaker.
5. After the beaker cools, add 2 ml of 16 M HNO₃ and evaporate to dryness. Repeat treatment until all organic matter is destroyed. Four or five evaporation are usually required.
6. Add 5 ml of 70% HClO₄ and evaporate to dense fumes. Separate the K by treatment with ethyl acetate (Note 2 and 3). Dissolve the

PROCEDURE 5 (Continued)

precipitate in water and 5 mgs Na carrier and precipitate the K as the perchlorate. Filter and dissolve the precipitate in water. Add 5 mg of Na and 1 drop of HClO_4 . Evaporate the solution to dryness. Then carry out a final precipitation of K from ethyl acetate. Dry at 110°C for 20 minutes and ignite at 300°C for 20 minutes. Weigh as KClO_4 to determine the chemical yield.

7. The K_2CO_3 comparator is carried through the same procedure as the Mg sample.

C. Measurement of K^{42} Radioactivity

1. The activity of the K^{42} may be measured by beta or gamma counting.

Use a Geiger-Mueller counter for beta measurements and a gamma scintillation counter for the gamma measurements.

2. Following the radioactivity measurements, correct the K^{42} activity for decay, dilution volume, and sample and yield weights for both the magnesium and standard samples. A ratio of these corrected radioactivities becomes a measurement of the stable potassium in the sample:

$$\% \text{K in Sample} = \frac{\text{Corrected } \text{K}^{42} \text{ in Mg sample}}{\text{Corrected } \text{K}^{42} \text{ in standard sample}} \times 100$$

Notes:

1. A 24-hour irradiation would be sufficient if the analyst can obtain the sample within a day after irradiation.

2. Page 8 in "Applied Inorganic Analysis" by W. F. Hillebrand and G. E. F. Lundell - 1929.

3. The filtrate from the K precipitate may be saved for Na analysis if desired; however, the analyst must remember that Na^{24} can also be formed by the fast neutron reaction, $\text{Mg}^{24}(\text{n},\text{p})\text{Na}^{24}$. The authors found that a Mg sample with 10 ppm of stable Na present analyzed 123 and 116 ppm by activation.

PROCEDURE 6

Procedure Used In: Radioactivation analysis

Method: Precipitation

Element Separated: K⁴² (12.4 h)

Type Material Bombarded: Dunite mineral ore from Balsam Quarry, North Carolina

Type Nuclear Bombardment: K⁴¹(n, γ)K⁴²

Procedure By: Salmon (133)

Separation Time: Not estimated by author

Chemical Yield of Carrier: Approximately 75%

Equipment Needed: Standard

Procedure:

1. Weigh approximately 50 mg of sample into a short length of polythene tubing and heat seal the ends. Similarly, weigh and seal 20 mg of K₂CO₃ dried at 110° C as a standard. Irradiate sample and standard in BEPO (at Harwell) for about 3 hours.
2. After the irradiation, empty the sample into a platinum dish containing 5 ml of a solution of KCl as carrier (10 mg of K⁺ per ml). Add a few drops of H₂SO₄ (SpG 1.84) and 10 ml of 40% HF. Evaporate gently to fumes of H₂SO₄, cool and add 10 ml of HF and again evaporate to fumes. Cool the residual solution and transfer it to a 250-ml beaker with H₂O.
3. Add 10 ml of HNO₃ (SpG 1.42) and 5 ml of HClO₄ (SpG 1.70). Heat until strong HClO₄ fumes appear, then cool to room temperature. Transfer the solution and precipitated KClO₄ to a 50-ml centrifuge tube using absolute ethanol for rinsing. Centrifuge and wash the precipitate three times with ethanol. Dissolve the precipitate with 10 ml of H₂O.
4. At this step, take a suitable aliquot from the irradiated standard and to it add 5 ml of potassium carrier and continue with the separation for both sample and standard.
5. Add 10 mgs of Fe⁺³ or chloride, stir and make basic with NaOH. Centrifuge the Fe(OH)₃ and filter the supernate into another 50-ml centrifuge tube.
6. Just acidify the filtrate with glacial acetic acid and add an

PROCEDURE 6 (Continued)

excess of freshly prepared 10% aqueous solution of sodium cobaltinitrite.

Allow the precipitate to settle and centrifuge. Discard the supernate.

Wash the precipitate three times with water.

7. Dissolve the precipitate with 2 ml dilute HNO_3 (1 + 1) with gentle heat. Cool and add 2 ml of dilute HNO_3 and 15 ml of absolute ethanol.

Precipitate the potassium chloroplatinate with 1 ml of 10% w/v platinum chloride solution. Centrifuge and wash 3 times with ethanol.

8. Make a slurry with a small quantity of ethanol and transfer it to a weighed counting container, dry it under an infra-red lamp and weigh for chemical yield determination.

9. Determine the K^{42} either by beta or gamma measurement (Note 1).

$$\text{Wt of K in sample} = \frac{(\text{Wt of K in standard}) (\text{Sample activity})}{\text{Standard activity}} \quad (\text{Note 2})$$

Notes:

1. Author measured beta radioactivity.

2. Author found 0.0032% K; Na content of sample: 0.011%.

PROCEDURE 7

Procedure Used In: Radioactivation analysis

Method of Separation: Precipitation (See Note 1)

Element Separated: K^{42} (12.4 h)

Type of Material Analyzed: Water, ⁽¹³²⁾ aluminum, stainless steel, soils, vegetation, ore concentrates, clays, limestone, cement tissue, resins, lithium carbonate, and lithium iodide. ^(136,137)

Type of Nuclear Bombardment:

Procedure By: Leddicotte ^(136,137)

Chemical Yield of Carrier: At least 65%

Time of Separation: 2 hours

Degree of Purification: Greater than 10^5 from radionuclides of Na, Cu, Mn, Fe, Co, and Zn.

Equipment Required: Standard

PROCEDURE 7 (Continued)

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 2) and comparator (Note 3) samples in a neutron flux of at least 6.5×10^{11} n/cm²/sec for 16 hours or longer (Note 4). Prepare the test and comparator sample for the irradiation either by wrapping each specimen in aluminum foil or placing it in quartz ampoule. Liquid samples should be irradiated in polyethylene bottles (Note 5).

B. Preparation of Irradiated Materials for Analysis

I. The Comparator Sample

1. After the irradiation, quantitatively transfer the comparator sample (Note 3) to a 50-ml volumetric flask. Dissolve the sample in a small, measured volume of 6 M HNO₃; then dilute the solution to 50 ml with water. Mix the solution well by carefully shaking it.

2. By means of a volumetric pipet, pipet a 1.00-ml aliquot of this solution into a 100-ml volumetric flask; then dilute the aliquot to 100 ml with water.

3. Shake the solution thoroughly; then pipet a 1.00-ml aliquot of it into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same centrifuge tube, 2.00 ml of a standard carrier solution of known potassium concentration (Note 6). Also, add 1 ml each of holdback carriers of barium, cadmium, cobalt, copper, iron, manganese, phosphorus, sodium, and zinc (Note 7). Dilute the solution to 20 ml with water, mix it well and make the solution 0.3 M in HCl. Continue with Part C below.

II. Solid Test Sample

1. If the sample is a metal or alloy, quantitatively transfer the irradiated test portion from the quartz tube or aluminum wrap to a 50-ml glass centrifuge tube, and then add, by means of a volumetric pipet, to the same centrifuge tube 2.00 ml of a standard carrier solution of known potassium concentration (Note 6). Also add 1 ml each of holdback carriers of barium, cadmium, cobalt, copper, iron, manganese, phosphorus, sodium, and zinc (Note 7). To this mixture, add dropwise enough concentrated mineral acid

PROCEDURE 7 (Continued)

to completely dissolve the sample (Note 8). Dilute the solution to 20 ml with water, mix it well and make the solution 0.3 M in HCl. Continue with Part C below.

III. Liquid Test Samples

1. Pipet an aliquot of the irradiated portion into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same centrifuge tube 2.00 ml of a standard carrier solution of known potassium concentration (Note 6). Also add 1 ml each of holdback carriers of barium, cadmium, cobalt, copper, iron, manganese, phosphorus, sodium, and zinc (Note 7). Dilute the solution to 20 ml with H_2O , mix it well, and make the solution 0.3 M in HCl. Continue with Part C below.

IV. Organic Test Samples

1. If the sample is a tissue, vegetation, or a similar material, quantitatively transfer the irradiated test portion from the irradiation container to a 50-ml beaker. By means of a volumetric pipet, add to the same beaker 2.00 ml of a standard carrier solution of known potassium concentration (Note 6). Also add 1 ml each of holdback carriers of barium, cadmium, cobalt, copper, iron, manganese, phosphorus, sodium, and zinc (Note 7). Then add 3 ml of conc. H_2SO_4 and 4 ml of conc. HNO_3 . Cover the beaker with a watch glass; then boil the solution for 15 minutes. Cool the solution, add to it 3 ml more of conc. HNO_3 , and boil the solution for 15 minutes (or to fumes of SO_3). Repeat the addition of HNO_3 and the boiling until the sample is dissolved. Add a few ml of conc. HCl, evaporate to remove HNO_3 . Repeat several times if necessary. Dilute solution to make it 0.3 M in HCl. Transfer to a 50-ml centrifuge tube; then continue with Part C below using the procedure described, either as I. By the Chloroplatinate Method,⁽¹³⁷⁾ or as II. By the Perchlorate Method.⁽¹³⁸⁾

C. Radiochemical Separation of K⁴²

I. By the Chloroplatinate Method

1. Saturate the solution with H_2S . Centrifuge the mixture (Note 9).

PROCEDURE 7 (Continued)

Transfer the supernatant liquid to a new 50-ml centrifuge tube. Wash the precipitate with one 10-ml portion of hot water. Centrifuge the mixture and add the wash to the centrifuge tube. Discard the precipitate.

2. Add 3 ml of bromine water to the supernatant liquid-water wash mixture. Boil until all of the excess H_2S has been removed; then add conc. NH_4OH dropwise until no further precipitation of $Fe(OH)_3$ occurs. Centrifuge the mixture (Note 10). Filter the supernatant liquid into a new 50-ml centrifuge tube. Discard the $Fe(OH)_3$ precipitate.

3. Heat the solution to near boiling; add a 1-2 ml volume of barium holdback carrier and add dropwise enough saturated ammonium carbonate solution until no further precipitation of $BaCO_3$ occurs. Heat the mixture to boiling and allow the precipitate to settle. Centrifuge the mixture (Note 11). Filter the supernatant liquid into a small porcelain evaporating dish. Wash the precipitate once with hot water (Note 12) and then centrifuge. Filter the supernatant liquid into the evaporating dish.

4. By use of a hot plate, or a heat lamp, slowly concentrate the solution by evaporating the solution to a 1-ml volume; then add 1-2 ml of conc. HCl and 2 ml of chloroplatinic acid to the dish (Note 13).

5. Repeat the evaporation process until the mixture becomes syrupy (Note 14). Cool until the mixture becomes solid.

6. Add 2 ml of 95% ethyl alcohol (Note 15) and then crush the solid with a glass stirring rod. Allow the mixture to stand for 30 minutes (Note 16).

7. Filter off the K_2PtCl_6 precipitate through a tared filter paper (Munktells No. 00) that is held in a Hirsch funnel (Note 17); wash the precipitate three times with 5-ml portions of 95% ethyl alcohol. Dry the precipitate for 1 hour in a drying oven at $110^\circ C$. Cool in a dessicator. Weigh the K_2PtCl_6 precipitate and filter paper on an analytical balance. Mount the precipitate and count its radioactivity as instructed in Part D below.

II. By the Perchlorate Method

1. Add 10 ml of 70% $HClO_4$ to the solution in the centrifuge tube. Place the tube into an ice bath. Cool at this temperature ($20^\circ C$) for

PROCEDURE 7 (Continued)

at least 30 minutes or until no further precipitation of ClO_4^- ions occur (Note 18). Centrifuge the mixture; discard the supernatant liquid. Wash the ClO_4^- precipitate with 5 ml of 95% ethyl alcohol. Stir vigorously while adding the alcohol. Centrifuge and discard the wash liquid.

2. Add 1-2 ml of H_2O to the tube containing the ClO_4^- precipitate.

Warm slightly to complete the dissolution. Add additional volumes of the holdback carriers used previously. Concentrate the solution volume to 5 ml by boiling.

3. Repeat Step 1.

4. Repeat Steps 2 and 1 (in that order).

5. Filter off the KClO_4 precipitate through a tared filter paper (Munktells No. 00) that is held in a Hirsch funnel (Note 19); wash the precipitate three times with 5-ml portions of 95% ethyl alcohol and once with a 10-ml portion of ethyl ether. Weigh the KClO_4 precipitate and filter paper on an analytical balance; then mount and count its radioactivity as instructed in Part D below.

D. Measurement of K^{42} Radioactivity and Calculation
of Stable Potassium Content of Test Sample

1. The K^{42} radioactivity in both the test and the 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 20).

2. Following the radioactivity measurements, correct the observed K^{42} radioactivity for decay (Note 21), 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 potassium in the test sample:

$$\% \text{ K in Test Sample} = \frac{\text{Corrected } \text{K}^{42} \text{ radioactivity in Test Sample}}{\text{Corrected } \text{K}^{42} \text{ radioactivity in Comparator Sample}} \times 100.$$

Notes:

1. This procedure describes the precipitation of potassium either as

PROCEDURE 7 (Continued)

$KClO_4$ or K_2PtCl_6 . The techniques concerned with sample irradiation, processing of irradiated material, and the measurement of K^{42} (12.4 h) radioactivity apply in either application.

2. Solid test samples should weigh from 0.10 - 0.20 gram; liquid samples should have a volume of from 5 - 25 milliliters.

3. Use 0.025 to 0.030 grams of spectrographically pure K_2CO_3 .

4. The limits of measurement for stable potassium by this procedure is 1×10^{-7} gram.

5. Irradiations of liquid, vegetation, or similar type sample materials must be made in an air-cooled or water-cooled reactor irradiation facility.

6. Standardized to contain at least 10 milligrams of potassium per milliliter.

7. Solutions of the ions of other elements may also be added as holdback carriers; concentration equal to 5 milligrams of element per milliliter.

8. Soils, clays, and similar materials may require addition of HNO_3 or fusion.

9. Additional amounts of Cu^{+2} ions may be added here for further scavenging of acid sulfide precipitable elements. Sufficient H_2S is present to cause CuS precipitation. Centrifugation is advisable after each addition of copper holdback carrier.

10. Additional amounts of Fe^{+3} ions may be added here to serve as a scavenger for other hydroxide precipitable elements. Sufficient NH_3 ions are present to cause $Fe(OH)_3$ precipitation. Centrifugation is adviseable after each addition of iron holdback carrier.

11. The barium scavenging step may be repeated before centrifuging.

12. This step provides a means of removing adsorbed alkali chloride from the Br_2CO_3 precipitate.

13. This method is applicable for the determination of K in the presence of Na, Li, Mg, Ca, and Sr chlorides.

14. Complete evaporation will result in loss of potassium.

15. K_2PtCl_6 is slightly soluble in alcohols of less than 90%.

PROCEDURE 7 (Continued)

16. Additional alcohol will need to be added to the mixture during this time interval. Stir the mixture frequently.
17. The transfer from the evaporation dish is made by using small volumes of 95% ethyl alcohol.
18. Rubidium, if present, will also precipitate; sodium perchlorate will dissolve in 95% ethyl alcohol.
19. The $KClO_4$ precipitate may be washed from the centrifuge tube onto the filter paper with 95% ethyl alcohol.
20. Gamma-ray discrimination may be used here.
21. Decay measurements may be followed, if required.

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