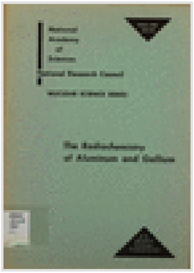

The Radiochemistry of Aluminum and Gallium (1961)

Pages
58

Size
6 x 9

ISBN
0309364884

Lewis, John Ernest; Subcommittee on Radiochemistry; Committee on Nuclear Science; National Research Council

COMMITTEE ON NUCLEAR SCIENCE

L. F. CURTISS, *Chairman*
National Bureau of Standards

ROBLEY D. EVANS, *Vice Chairman*
Massachusetts Institute of Technology

J. A. DeJUREN, *Secretary*
Westinghouse Electric Corporation

C. J. BORKOWSKI
Oak Ridge National Laboratory

ROBERT G. COCHRAN
Texas Agricultural and Mechanical College

SAMUEL EPSTEIN
California Institute of Technology

U. FANO
National Bureau of Standards

HERBERT GOLDSTEIN
Nuclear Development Corporation of America

J. W. IRVINE, JR.
Massachusetts Institute of Technology

E. D. KLEMA
Northwestern University

W. WAYNE MEINKE
University of Michigan

J. J. NICKSON
Memorial Hospital, New York

ROBERT L. PLATZMAN
Laboratoire de Chimie Physique

D. M. VAN PATTER
Bartol Research Foundation

LIAISON MEMBERS

PAUL C. AEBERSOLD
Atomic Energy Commission

J. HOWARD McMILLEN
National Science Foundation

CHARLES K. REED
U. S. Air Force

WILLIAM E. WRIGHT
Office of Naval Research

SUBCOMMITTEE ON RADIOCHEMISTRY

W. WAYNE MEINKE, *Chairman*
University of Michigan

GREGORY R. CHOPPIN
Florida State University

GEORGE A. COWAN
Los Alamos Scientific Laboratory

ARTHUR W. FAIRHALL
University of Washington

JEROME HUDIS
Brookhaven National Laboratory

EARL HYDE
University of California (Berkeley)

HAROLD KIRBY
Mound Laboratory

GEORGE LEDDICOTTE
Oak Ridge National Laboratory

JULIAN NIELSEN
Hanford Laboratories

ELLIS P. STEINBERG
Argonne National Laboratory

PETER C. STEVENSON
University of California (Livermore)

LEO YAFFE
McGill University

CONSULTANTS

NATHAN BALLOU
Naval Radiological Defense Laboratory

JAMES DeVOE
University of Michigan

WILLIAM MARLOW
National Bureau of Standards

CHEMISTRY

The Radiochemistry of Aluminum and Gallium

JOHN E. LEWIS

Aluminum Company of America
Alcoa Research Laboratories
Physical Chemistry Division
New Kensington, Pennsylvania

Issuance Date: April 1961

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

Printed in USA. Price $0.50. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

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 aluminum and gallium 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.

Two considerations dictated the decision to treat aluminum and gallium jointly in this monograph. First, and perhaps the most important, was the over-all similarity in the chemistries of the elements. Secondly, a cursory survey of the radiochemical applications of isotopes of the elements revealed appreciably more specific applications of isotopes of gallium than aluminum and it was felt that neither element warranted individual attention in separate monographs.

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 aluminum and gallium which might be included in a revised version of the monograph.

CONTENTS

The Radiochemistry of Aluminum and Gallium

JOHN E. LEWIS
Aluminum Company of America
Alcoa Research Laboratories
Physical Chemistry Division
New Kensington, Pennsylvania

I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF ALUMINUM AND GALLIUM

(1) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London (1950).

(2) W. R. Schoeller and A. R. Powell, "The Analysis of Minerals and Ores of the Rarer Elements," 3rd Edition, Hafner Publishing Company, New York (1955).

(3) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Edition, John Wiley and Sons, Inc., New York (1953).

(4) W. D. Wilkinson, "Properties of Gallium," Argonne National Laboratory Report No. ANL-4109 (1948).

(5) Erich Einecke, "Das Gallium," Verlag von Leopold Voss, Leipzig (1937), Lithoprint Edition by J. W. Edwards, Ann Arbor, Michigan (1944).

(6) J. Dolezal, V. Patrovsky, Z. Sulcek and J. Svasta, "Analytical Chemistry of Gallium," Chem. Listy 40, 1517 (1955).

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF ALUMINUM AND GALLIUM

At this writing, the author is not aware of any publication which qualifies to be classified as a review of the radiochemistry of either aluminum or gallium. However, a series of articles authored by Rightmire and associates,(1,2,3,4) pertaining to the identification of long-lived Al^{26} isotope, deserves special mention in this category.

III. TABLES OF ISOTOPES

The most significant recent contribution to the field of aluminum radiochemistry was the discovery, by Simanton et al.,(1) of the long-lived Al^{26}, isomeric with the metastable 6.6 sec. isotope. As the authors point out, until the time of the discovery in 1954, aluminum was the only element devoid of a suitable isotope for tracer experiments. The half-lives of the Al^{28} and Al^{29} isotopes are sufficiently long to permit their use in specific applications such as activation analysis, but this use has been confined to laboratories fortunate enough to have their own irradiation facilities. Currently a number of manufacturers are offering laboratory size neutron sources and it is anticipated that short-lived isotopes such as Al^{28} and Al^{29}

will find increased application in future radiotracer investigations.

Table I

ISOTOPES OF ALUMINUM*

	Half-Life	Type of Decay	Energy of Radiation	Some Typical Modes of Formation
Al^{23}	.13 sec.			
Al^{24}	2.1 sec.	β^+ γ	~8.5 1.38 - 7.1	Mg^{24} (p,n)
Al^{25}	7.6 sec.	β^+	3.2	Mg^{25} (p,n)
Al^{26m}	6.6 sec.	β^+	3.2	Mg^{25} (d,n) Mg^{26} (d,2n)
Al^{26}	8 x 10^5 y	ec β γ	 1.16 1.83,1.14	Mg^{25} (d,n) Mg^{26} (p,n) Al^{27} (n,2n)
Al^{27}	100% Abundance (Stable)		-----	
Al^{28}	2.27 min.	β^- γ	2.86 1.78,1.27	Al^{27} (n,γ) Al^{27} (d,p) P^{31} (n,α)
Al^{29}	6.56 min.	β^- γ	2.5,1.4 1.28,2.43	Al (α,2p) Mg (α,p)

* Data obtained from the following sources:

(A) Friedlander, G. and Kennedy, J. W., "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York (1955).

(B) Strominger, D., Hollander, J. M. and Seaborg, G. T., "Table of Isotopes," Reviews of Modern Physics <u>30</u>, No. 2, 585 (1958).

Table II

ISOTOPES OF GALLIUM*

	Half-Life	Type of Decay	Energy of Radiation	Some Typical Modes of Formation
Ga^{64}	2.6 min.	β^+	~5	Zn^{64} (p,n)
		γ	0.97,2.2,3.8	(d,2n)
Ga^{65}	15 min.	β^+	2.2	Zn^{64} (d,n)
		$e^-\gamma$	0.052	
Ga^{65}	8 min.	β^+	-----	
		γ	0.092,0.114	
Ga^{66}	9.4 hrs.	β^+	4.14	Zn^{66} (d,2n)
				(p,n)
		ec	-----	Cu^{63} (α,n)
		γ	0.83 to 4.83	
Ga^{67}	78 hrs.	ec	-----	Zn^{66} (d,n)
		γ	0.09 to 0.9	
Ga^{68}	68 min.	β^+	1.88	Zn^{68} (d,2n)
		ec		Cu^{65} (α,n)
		γ	1.10	Ge^{70} (d,α)
Ga^{69}	60.5% Abundance (Stable)			
Ga^{70}	21.4 min.	β^-	1.65	Ga^{69} (n,γ)
				Ga^{69} (d,p)
		γ	0.17,1.04	Ge^{70} (n,p)
Ga^{71}	39.5% Abundance (Stable)			Ge^{72} (d,α)
Ga^{72}	14.2 hrs.	β^-	0.6, 0.9,	Ga^{71} (d,p)
			1.5,2.5,3.1	Ga^{71} (n,γ)
		γ	0.84,2.508,2.491 plus others	Ge^{72} (n,p)
Ga^{73}	5.0 hrs.	β^-	1.4 (to Ge^{73m_2})	Ge^{73} (n,p)
Ga^{74}	8 min.	β^-	1.1,2.0,2.65	Ge^{74} (n,p)
		γ	0.60,2.3,others	Ge^{74} (n,f)

* Data obtained from the following sources:

(A) Friedlander, G. and Kennedy, J. W., "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York (1955).

(B) Strominger, D., Hollander, J. M. and Seaborg, G. T., "Table of Isotopes," Reviews of Modern Physics <u>30</u>, No. 2, 585 (1958).

IV. REVIEW OF THOSE FEATURES OF ALUMINUM AND GALLIUM CHEMISTRY OF CHIEF INTEREST TO THE RADIOCHEMIST

A. Metallic State

Aluminum is the most abundant of all metals (8.1%) and ranks third in abundance of all the elements. By contrast, gallium is relatively scarce (abundance 1.5 x 10^{-3}%), although it occurs widely distributed in nature. Germanite is credited with being the richest known source of gallium. Gallium occurs in trace amounts (estimated at a few thousandths of one per cent) in bauxite, but significant quantities of the element become concentrated in the caustic liquors during processing of the bauxite to yield alumina.

While a description of the physical appearance of aluminum is unwarranted, the appearance of gallium deserves brief mention. In the laboratory, gallium may be encountered in either a liquid or solid state because of its low melting point of approximately 29.8°C. Both solid and liquid gallium exhibit a blue-grey coloration associated with a thin protective oxide film on the surface. Both aluminum and gallium quickly acquire a relatively impervious oxide film upon exposure to air, which accounts for their ability to resist further oxidation and chemical attack.

Gallium is remarkable in its ability to undergo supercooling and will remain indefinitely in a liquid state even at ice temperatures. Gallium, like bismuth, expands on freezing. The volume change on solidification is about 3%. Selected properties of aluminum and gallium are listed in Table III.

Table III*

Property	Aluminum	Gallium
Atomic Number	13	31
Mass Numbers, Stable Isotopes	27	69, 71
Density of Solid at 20°C, g/cc	2.70	5.93
Melting Point °C	659.8	29.78
Boiling Point °C	2270	2070
Ionization Potential, ev	5.984	6.00
Crystal Radius M^{+3}, Å	0.50	0.62

* Therald Moeller, "Inorganic Chemistry," John Willey and Sons, Inc., New York (1952).

Aluminum and gallium are amphoteric elements, behaving as metals in acid and as nonmetals in alkaline media. Commercially pure aluminum is soluble in dilute mineral acids and, in general, the rate of dissolution increases with increasing acid concentration and temperature, except in nitric acid where aluminum remains relatively passive. Superpure aluminum dissolves slowly in concentrated HCl but the solution rate can be markedly increased with the addition of concentrated HNO_3 or a trace of mercury salt. Caustic solutions dissolve aluminum readily.

Gallium is difficultly soluble in mineral acids but hot aqua regia sustains dissolution at a respectable rate. Foster(5) reports rapid solution of gallium in a mixture of two-thirds concentrated H_2SO_4 and one-third perchloric acid (72%). Foster and Stumpf(6) discuss the electrolytic solution of gallium in hot nitric acid in a platinum container. As in the case of aluminum, gallium dissolves readily in strong alkali solutions.

Although gallium is recognized as existing in three valence states (i.e., +1, +2 and +3), the trivalent compounds of gallium are of primary interest to the radiochemist. Similarly, trivalent aluminum is normally encountered in procedures pertinent to radiochemical work.

B. Compounds of Aluminum and Gallium

While aluminum and gallium form numerous compounds with various organic and inorganic reagents, only those compounds which are of interest from a radiochemical standpoint will be considered here.

Hydroxides and Oxides

Ammonium and alkali hydroxides precipitate aluminum and gallium hydroxides (hydrated oxides) upon neutralizing acid solutions of the trivalent salts of the elements. The hydroxides show limited solubility in excess ammonium hydroxide but alkali hydroxides completely dissolve the precipitates to form aluminates and gallates.

The gelatinous nature of the hydroxide precipitates is sometimes objectionable and precipitants such as tannin, ammonium bisulfite and sodium thiosulfate may be employed to obtain a more granular product. In analytical practice, it is customary to use aluminum and gallium hydroxides only as intermediate products in an analysis sequence since the hydroxides are capable of carrying down a host of contaminating elements.

While aluminum and gallium form oxides of the types described by the general formulas Mo, M_2O and M_2O_3, only the sesquioxides (Al_2O_3 and Ga_2O_3) are of interest to the radiochemist. The sesquioxides are frequently the final product in gravimetric procedures involving the ignition of hydroxides or organic precipitates such as cupferrates and quinolates. Ignition of the oxides is usually performed at temperatures in excess of 1000°C to provide products which are completely nonhygroscopic. Special care must be exercised in igniting organic compounds of gallium to prevent the loss of gallium as the volatile suboxide (Ga_2O) resulting from the reduction of the sesquioxide by traces of unconsumed carbon.

Halides

The halides of gallium (fluoride is the exception) are hygroscopic and undergo hydrolysis in aqueous solution. The dichlorides and dibromides disproportionate at elevated temperatures to yield the respective trihalides plus free metal. Of the trihalides, $GaCl_3$ is of primary interest in analytical radiochemistry.

Anhydrous $GaCl_3$, formed by reacting the metal with dry hydrogen chloride or chlorine gases, volatilizes at a relatively low temperature (b.p. 201°C) and sublimes. This property can be used to advantage as a means of purifying the compound or separating it from less volatile species. While the loss of gallium as the chloride is presumably nil during evaporations of acid solutions of the salt, loss may occur during the ignition of gallium bearing compounds.(5)

In a hydrochloric acid solution of the chloride, gallium exists as the $GaCl_4^-$ ion which is extractable into various organic solvents and shows strong adsorbability by anion exchange resins such as Dowex-1. Aluminum does not form a similar chloride complex and this depature from the general similarity in the chemistry of the elements permits their separation from each other via solvent extraction and ion exchange techniques.

Among the halides of aluminum, $AlCl_3$ is of primary interest. Like its gallium counterpart, anhydrous $AlCl_3$ is produced by reaction of the metal with gaseous hydrogen chloride or chlorine. $AlCl_3$ volatilizes readily and sublimes at approximately 178°C.

Hydrated aluminum chloride, $AlCl_3 \cdot 6H_2O$, resists attack in concentrated hydrochloric acid and $AlCl_3$ precipitation can be used to separate aluminum from iron and beryllium. (See Section C)

Sulfides

The literature lists three stable sulfides of gallium, namely Ga_2S, GaS and Ga_2S_3, and only one sulfide of aluminum, Al_2S_3. These sulfides form by reacting the metals with hydrogen sulfide or sulfur vapors at elevated temperatures and are of little interest to the analyst.

Aluminum and gallium do not form sulfides when their solutions are gassed with hydrogen sulfide. However, small amounts of gallium can be separated adsorptively from weakly acid solutions containing elements precipitable by H_2S. Arsenic sulfide, in particular, is an excellent "getter" for small amounts of gallium.

C. Gravimetric Separations

Both aluminum and gallium are precipitated as hydroxides with ammonia in the familiar "R_2O_3" group separation scheme. A number of elements including iron, titanium, zirconium, rare earth metals etc. accompany aluminum and gallium in the precipitate such that separations by this method usually serve only as an intermediate step in radiochemical analysis schemes.

The determination of impurity elements in aluminum and gallium by activation analysis frequently requires the removal of the matrix element to facilitate the separation of the element(s) of interest. The removal of aluminum as the hydroxide is unsuitable because the voluminous, gelatinous precipitate may carry down elements by coprecipitation or entrainment. A procedure suggested by Gooch and Havens(7) involving the precipitation of aluminum as $AlCl_3 \cdot 6H_2O$ from a cold hydrochloric acid-ether solution, provides a crystalline product which is comparatively free of coprecipitated contaminants. This procedure can be employed in separating aluminum from gallium.

Aluminum may be precipitated as the phosphate from a dilute acetic acid-sodium acetate solution with excess $(NH_4)_2HPO_4$ but elements such as iron, titanium and others will be found in the precipitate.

Phenyhydrazine is a useful precipitant for separating aluminum from divalent iron and other elements which accompany it in the ammonia group precipitation procedure.

8-hydroxyquinoline precipitates aluminum quantitatively in the pH range of 4.2 to 9.8.(8) The precipitate, $Al(C_9H_6NO)_3$, can be weighed directly or ignited to the sesquioxide, Al_2O_3. The method is not specific in either acidic or alkaline media and prior knowledge of possible contaminating elements is desirable. Gallium is also precipitated by this reagent and its use in radiochemical separations has become widespread. (See Procedures 3, 5, 6 and 9 in Section VII)

Cupferron will precipitate gallium quantitatively from dilute H_2SO_4 solution (approximately 10% by volume) using an excess of reagent. The gallium is collected as Ga_2O_3 following ignition of the cupferrate.

Hopkins(9) reports the separation of gallium from zinc, cadmium, cobalt and others with camphoric acid or sodium camphorate additions to acetic acid solutions.

Gallium can be separated from aluminum and chromium by precipitation as the ferrocyanide. Zinc, which would precipitate with gallium from acid solution, requires prior separation. Following ignition of the ferrocyanide precipitate, the iron can be removed by familiar techniques and the gallium reprecipitated as the hydroxide.

D. Solvent Extraction Separations

1. Chelate Complexes

a. Acetylacetone

Aluminum and gallium form extractable chelates with acetylacetone. Steinbach and Freiser(10) describe the extraction of aluminum and gallium by acetylacetone in chloroform at pH's of 4 and 2, respectively.

Wold et al.(11) used acetylacetone to extract 90% of the gallium from 61% HCl solution of aluminum and gallium. Ga-acetylacetonate crystals were identified by microscopic examination to distinguish gallium from aluminum.

b. Thenoyltrifluoroacetone (TTA)

Bolomay and Wish(12) report the extraction of aluminum at pH 5.5 by 0.02M TTA in benzene. Eshelman(13) observed that aluminum is selectively extracted from an acetate-buffered solution of pH 5.5 to 6.0 with 0.1M 2-thenoyltrifluoroacetone (TTA) in 4-methyl-2-pentanone. Alternatively, an acetate-buffered solution of pH 2.5 to 4.5, containing cupferron with 4-methyl-2-pentanone, was used.

c. Morin (3,5,7,2,4-pentahydroxyflavone)

Morin reacts with both aluminum and gallium in acidic media to form complexes that are extractable by amyl, butyl and cyclohexyl alcohols.(14)

d. 8-Quinolinol (Oxine)

Although aluminum and gallium form extractable complexes with 8-quinolinol, the extractions are not selective and are subject to contamination by interferring ions.

Luke and Campbell(15) determined gallium and germanium and germanium dioxide by ether extraction from 6N HCl, followed by an oxine-chloroform extraction from alkaline cyanide solution. Gallium was determined photometrically in the yellow oxine-chloroform extract.

Kambara and Hoshitani(16) discuss the theory for extraction of aluminum oxinate by chloroform.

Moeller and Cohon(17) report that gallium (as oxinate) can be extracted completely from acetate-buffered (pH 3.0 to 6.2) salt solutions by shaking with chloroform solutions of 8-hydroxyquinoline.

Lecroix(18) demonstrated that one part of gallium could be separated from 10^4 parts of aluminum by extraction as the oxinate at pH-2 into chloroform.

e. Cupferron (Ammonium Salt of N-nitrosophenylhydroxylamine)

The extraction of aluminum as the cupferrate into chloroform has been investigated by Meunier(19) and Bandisch and Furst.(20)

f. Sodium Diethyldithiocarbamate

Cherniko and Kobkina(21) report the extraction of the gallium complex at pH-3 into a ethyl acetate employing excess acetate to preclude decomposition of the complex. The extraction of aluminum and gallium via complex formation with the above reagents is not necessarily selective or quantitative and the reader is cautioned to refer to the original publications to determine the suitability of a particular reagent for a specific application.

2. Ion Association Complexes

The extraction of metallic elements is made possible by the formation of a metal complex in the aqueous phase via an ion pairing mechanism. As an example, in the case of gallium, the consensus is that gallium forms an extractable complex via incorporation of the metal in the anionic partner of the ion pair (H^+, $GaCl_4^-$).

Milner et al.(22) investigated the extractability of gallium halides from acid solutions with organic solvents and observed that the chloride was extracted more efficiently than either the bromide or iodide. It was also found that extraction of the chloride was as efficient using ketones as the customary diethyl ether solvent, but ether was preferred in their work involving gallium-uranium mixtures. The gallium was recovered by precipitation with camphoric acid after buffering the solution with formic acid-ammonium formate buffer of pH-3.3.

Bach and Herrman(23) have investigated the extraction of Al (III) and Ga (III) as fluoride complexes from 20M HF into ethyl ether. The Al (III) and Ga (III) showed negligible extraction (i.e. 0.2% and <0.05%, respectively).

The extraction of chloride complexes from HCl solutions into various organic solvents has received considerable attention. While aluminum is not amenable to separation by this procedure, the extraction of gallium is excellent, as indicated in the following tabulation:

	Aqueous	Organic	Per Cent Extraction	Reference
Ga III	6M HCl	Ethyl Ether	97	(24)
	7M HCl	Isopropyl Ether	>99.9	(25)
	3M HCl	Tributylphosphate	99.9	(26)

Additional elements such as Sb (V), As (III), Fe (III) and Au (III), to mention a few, are likely to extract with the gallium.

The extractability of a number of metal bromides into ethyl ether has been investigated by Bock et al.(27)

While Al (III) was observed to extract to a negligible extent, 95 to 97% extraction of gallium from 5 to 6M HBr solution was found. As is the case of chloride extraction, the gallium would be accompanied by a variety of contaminants such as In (III), Sb (V) and Fe (III).

The extraction of aluminum and gallium as iodides has not looked promising. Kitachara(28) found no extraction of aluminum or gallium from 6.9M HI solutions into ethyl ether.

Bock(29) has made a comprehensive investigation of the extraction of metal thiocyanates into ethyl ether as a function of NH_4SCN concentration. Al (III) showed a maximum extraction (approximately 19%) from 6M HN_4SCN while Ga (III) exhibited >99% extraction from 7M HN_4SCN. It is suggested that best results are obtained when the HCl concentration in the aqueous phase is 0.5M.

Johnson(30) has observed that aluminum and gallium benzoates are extractable by ethyl acetate or butyl or amyl alcohol. Sundaram and Banerjee(31) report essentially complete extraction of aluminum by chloroform from aqueous butyric acid at pH of 9.3 to 9.5.

White(32) reported complete extraction of Ga (III) from 7M HCl with tri-n-actylphosphine oxide. (0.1M in cyclohexane.) Complete extraction of Al (III) was affected from 7M HCl using a 0.1M solution of tris-2-ethyl-n-hexylphosphine oxide. A variety of other elements accompany aluminum in both extraction procedures.

The majority of the material presented in this section on solvent extraction was taken from the book by Morrison and Freiser.(33)

E. Ion Exchange Separations

The ion exchange approach to chemical separations is ideal for trace element partitions often required in radiochemical work. Aluminum and gallium are amenable to separation from each other and each in turn can be separated from a host of other elements by ion exchange techniques. The investigator has to choose between an anion or cation exchange procedure and experimental conditions will likely influence his decision.

Klement and Sandmann(34) utilized a cation exchange technique (Dowex-50 resin in H^+ form) to effect a separation of gallium, indium and germanium by elution with increasing concentrated HCl solutions. Indium was eluted with 0.4N HCl and the gallium was removed with 1.3N HCl. Strelow(35) reports the separation of Al (III) from Ti and Fe (III) in Dowex 50X8 by elution with 2N HCl. Titanium and iron elute prior to Al (III) with the same acid concentration. An Amberlite 1R-120 column in the H^+ form was employed by Kejima and Kakihana(36) to separate iron and aluminum. The iron was eluted with a 0.1N KI-0.15N KCl mixture and the aluminum removed with 2N HCl.

In recent years, anion exchange procedures have increased in use for effecting elemental separations previously assigned to cation exchange procedures. Many metallic elements exist (or may be converted to) as negatively charged complex ions in aqueous solution and these complexes are strongly adsorbed by various resins. Kraus and Nelson(37) discuss in detail the mechanics of the adsorbability of Ga (III) as the anion complex, $GaCl_4^-$, from HCl solution.

Kraus, Nelson and Smith(38) showed that Al (III) undergoes negligible adsorption on Dowex-1 (strongly basic exchanger of the polystyrene-divinylbenzene type) while Ga (III) exhibits strong adsorption, the maximum occurring at an HCl concentration of 7M. The separation of Al (III), Ga (III), In (III) and Tl (III) on Dowex-1 was observed with the aid of Ga^{67}, In^{114} and Tl^{204} tracers. Al (III) and In (III) were eluted with 7<u>M</u> HCl [Al (III) appearing in the first 20 ml. of eluant and In (III) following in the next 50 ml.] while Ga (III) was eluted with 1<u>M</u> HCl and 4M $HClO_4$ was used to remove Tl (III).

The fact that Al is not adsorbed on anion exchange resins from halogen acid media has served as the basis for specific separations from adsorbable elements such as zirconium(39) and others.(40)

Kraus and Nelson(41) have examined the anion exchange behavior of the majority of elements in chloride media (HCl concentrations ranging from 0.1 to 12M). Faris,(42) in his investigation of the adsorption characteristics of some fifty elements on Dowex 1-X10 resin showed that Ga (III), as Ga^{67} tracer, exhibits negligible adsorption from 1, 2 and 4M HF. He reports a distribution coefficient of approximately 5.5 for Ga (III) in 0.4M HF. Al (III) shows a distribution coefficient of approximately 1.5 for 1M HF which decreases to zero at approximately 12M HF.

Marinsky and Eichler(43) and Gruverman and Kruger(44) give specific ion exchange procedures (see Section VII) for separating carrier free amounts of cyclotron produced gallium isotopes. Procedures 7 and 10 in Section VII include the use of ion exchange in the separation of Al^{26}.

F. Electrolytic Separations

The cathodic electrodeposition of gallium from aqueous solutions of its salts ($GaCl_3$, $Ga_2(SO_4)_3$, $NaGaO_2$) provides an efficient means of separating gallium from elements such as aluminum and sodium which do not deposit from aqueous media. While other elements, for example, indium, zinc and lead to mention a few, may codeposit with gallium, the number of interferring elements can be limited by controlled potential electrolysis and other selective electrolytic methods. A quantitative recovery of gallium by electrolysis may prove difficult to achieve but this is not a serious limitation in most radiochemical applications. Electrolysis, in conjunction with fractional crystallization, is a frequently used procedure for purifying gallium.(45)

V. DISSOLUTION OF SAMPLES CONTAINING COMPOUNDS OF ALUMINUM AND GALLIUM

A. Aluminum

1. Ores and Refractory Aluminous Materials

Bauxite is attacked readily by an $HF-H_2SO_4-HNO_3$ acid mixture. This is a preferred method when silica is to be eliminated and the presence of foreign salts is objectionable. In cases where silica is to be determined in bauxite or calcined refractories, dissolution via familiar fusion procedures (sodium carbonate, alkali pyrosulfate etc.) is to be recommended.(46) Bisulfate or carbonate-borax fusions conducted in platinum are familiar procedures for dissolving aluminum oxide.

2. Solution of Aluminum and Aluminum Alloys

Aluminum and its alloys can be dissolved in acid or alkaline hydroxide media and the choice of a solution procedure is usually dictated by the ultimate objective in mind. For instance, if the analyst is interested in determining silicon, an alkali attack of the sample is desirable, since acid decomposition may result in an incomplete oxidation of the silicon to silica and silicon losses due to silicon hydride formation may be encountered.

Solution of aluminum metal proceeds well in HCl, HF and other binary halogen acids. The attack of the metal by H_2SO_4, HNO_3 and other common inorganic acids used separately is slow, but solution in these media can be hastened by the addition of a pinch of mercury salt. A standard reagent(47) in the industry for dissolving the metal is a mixture of HCl, HNO_3 and H_2SO_4. The reaction of organic acids is, in general, rather slow and solution by organic reagents is not customarily utilized.

Aluminum is readily attacked by heating the metal in dry hydrogen chloride or oxygen-free chlorine with the formation of anhydrous aluminum chloride which sublimes at a relatively low temperature (slightly above 180°C).

High purity metal resists attack by HCl but a mercury salt may be used to accelerate the action. Aqua regia or sodium hydroxide are also effective reagents for high purity aluminum.

B. Gallium

1. Ores and Refractory Compounds

Gallium exists in trace quantities in a number of ores such as germanite, bauxite, various iron ores and zinc blende. As in the case of aluminum, the ores are attacked by acid or acid-mixtures, or the conventional salt flux fusion procedures may be utilized.

The sesquioxide of gallium, Ga_2O_3, is easily soluble in alkali hydroxide provided it has not been subjected to high temperatures during drying operations. If the oxide has been calcined at temperatures in excess of 1000°C, fusion procedures are necessary to render it soluble.

2. Gallium and Gallium Alloys

The solubility behavior of gallium, whether present in aluminum or magnesium alloys, is different in that in commercial aluminum, gallium exists in solid solution and dissolves in hydrochloric acid, while in magnesium the metal separates as globules which are not readily soluble in HCl.

In general, gallium is attacked most readily by aqua regia or alkaline hydroxides. Like aluminum, gallium will react with dry HCl or chlorine to form the anhydrous chloride which sublimes. Dennis and Bridgmann(48) adopted such a procedure for separating gallium from indium and zinc by volatilizing $GaCl_3$ in a stream of dry chlorine at 230-255°C (b.p. $GaCl_3$ - 215-220°C).

VI. COUNTING TECHNIQUES FOR USE WITH ISOTOPES OF ALUMINUM AND GALLIUM

A. Aluminum Isotopes

Refering to the table of aluminum isotopes (Section III) it is observed that the half-lives fall into two categories: six isotopes of half-life less than one hour, and one isotope with an extremely long half-life of approximately 8×10^5 years. For purposes of this discussion, only the isotopes of mass 26, 28 and 29 will be considered.

Aluminum^{28} ($t_{1/2}$ approximately 2.3 min.) decays by β^- emission (β^- 2.86 mev.) followed by the emission of a primary gamma ray of 1.78 mev. While this isotope can be assayed by a conventional Geiger-Mueller counting procedure, a gamma-ray scintillation spectrometer provides a rapid, discriminating counting procedure in view of the short half-life involved. Guinn and Wagner⁽⁴⁹⁾ describe an instrumental neutron analysis scheme for determining aluminum in a variety of materials employing a scintillation spectrometer.

Aluminum^{29} ($t_{1/2}$ = 6.56 min.) emits both beta and gamma rays and is amenable to assay by conventional detection devices. Spectrometers and proportional counters may be used to advantage for discriminately measuring its radiation in the presence of interfering activities.

The ground state Al^{26} isotope, with a half-life estimated at approximately 8×10^5 years,⁽²⁾ emits 1.16 mev. positrons, EC radiations and gamma rays with energies of 1.83, 2.97 and 1.14 mev. Kohman et al.⁽⁴⁾ describe the following assay procedures:

(1) Routine - positrons by Geiger and proportional counting procedures.
(2) Specific - gamma scintillation spectrometer for counting the 1.83 mev. gamma ray.
(3) Absolute - measure positrons in 4 pi counter.

(Sample enclosed in aluminized Mylar foil (1.0 mg./cm.^{2}) to exclude electron-capture radiations.)

B. Gallium Isotopes

It is seen from Table II that the majority of gallium isotopes decay with β and γ ray emissions which are sufficiently energetic to be assayed by conventional Geiger, proportional and scintillation counting procedures.

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES

Procedure 1

Gallium

Source: Ernst Bleuler and George J. Goldsmith, "Experimental Nucleonics," Rinehart and Company, Inc., New York (1952).

Reagents:
HCl - 5.45M, 0.3M, conc.
HNO_3 - conc.
NH_4OH - dilute
Ether -
H_2S -

Irradiation: Cu target (thin foil) bombarded with α particles for about 5 microampere minutes. Final sample weight 10 mg. or less. Activity - approximately 200 counts/sec.

Step 1 - Dissolve target in 1 ml. conc. HNO_3.

Step 2 - Add 3 ml. conc. HCl and evaporate to dryness. (Caution: low heat to avoid bumping.)

Step 3 - Saturate 25 ml. ether with 25 ml. 5.45M HCl by shaking in separatory funnel. Save both ether and acid portions.

Step 4 - Cool evaporated residue and add the acid used to saturate the ether.

Step 5 - Extract acid solution with three 1 ml. portions of ether to remove Cu and Ga. Combine ether fractions in clean separatory funnel.

Step 6 - Extract ether solution with 10 ml. 5.45M HCl to remove Cu which may have dissolved in ether layer because of the water which is dissolved in the ether.

Step 7 - Evaporate ether solution to dryness for gallium assay.

Step 8 - Evaporate aqueous solution to dryness; dissolve Cu salt in 15 ml. 0.3M HCl and saturate solution with H_2S.

Step 9 - Coagulate copper sulfide precipitate by heating, and filter on fine filter paper. Dry with alcohol, followed with ether.

Procedure 2

Gallium

Source: Same as for Procedure 1.

Reagents: See Procedure 1.

Irradiation: Deuteron bombardment of zinc foil target for several microampere minutes. Activity - approximately 200 counts/sec.

The chemical processing of the target to remove gallium activity duplicates Steps 1 through 7 of Procedure 1 except that the target is dissolved directly in HCl. Gallium is again removed by solvent extraction into ether. Zinc is precipitated from neutral solution with H_2S (HCl neutralized with NH_4OH) and the ZnS is assayed for zinc activity. The ether fraction containing gallium is evaporated to dryness for assay.

Procedure 3

Gallium

Source: J. A. Marinsky and E. Eichler, J. Inorg. Nucl. Chem. 12, 223 (1960).

Target: 2 ml. uranyl nitrate solution (approximately 850 mg. U/ml.).

Irradiation time: 2 minutes in Oak Ridge National Laboratory X-10 Reactor.

Step 1 - After 2 minute decay period to permit decay of very short-lived isotopes, solution is transferred to a separatory funnel containing 2 ml. (approximately 20 mg.) Ga carrier, 2 ml. (approximately 20 mg.) Ba carrier and 6 ml. 12M HCl.

Step 2 - Solution is contacted with 12 ml. of diisopropyl ether - 15 to 30 sec. (12.8 day Ba^{140} is separated from aqueous phase aliquot samples to provide fission-yield standard.)

Step 3 - Ga is back extracted into 10 ml. H_2O after washing ether layer with three 5 ml. portions of 6M HCl.

Step 4 - Solution is made 1M in HF and then passed through Dowex-1 anion exchange column (with the aid of compressed air to adsorb Mo). Effluent is collected in 5 ml. conc. HBr.

Step 5 - Acid mixture evaporated just to dryness. Residue is immediately dissolved in 10 ml. chilled 6M HCl and the Ga extracted with 10 ml. cold diisopropyl ether.

Step 6 - Ether extract is washed twice with 5 ml. portions of 6M HCl. Ga is back extracted into 10 ml. H_2O.

Step 7 - Aqueous sample is made 0.3M in HCl after addition of 10 mg. Bi and approximately 3 mg. Mo scavenger carriers.

Step 8 - Bi and Mo are precipitated with H_2S and precipitates are removed. Additional Mo is precipitated with α-benzoinoxime.

Step 9 - Filtrate is made slightly basic with 6M NH_4OH and Ga is precipitated with 8-hydroxyquinoline reagent.

Step 10 - Ga-8-hydroxyquinolate is filtered on paper disk for activity measurement.

Procedure 4

Gallium

Source: Irwin J. Gruverman and Paul Kruger, J. Applied Radiation and Isotopes 5, No. 1, 21 (1959).

Isotope: Ga^{67}

Target Material: Zinc

Product: 98+% Ga^{67} pure combined gallium activities in HNO_3 or HCl solution.

Product Reactions: Zn^{66} (d, n) Ga^{67}

Zn^{67} (d, 2n) Ga^{67}

Chemical Separation Principles: Ga is carried on $Fe(OH)_3$ from HN_4OH solution. Cu is retained in supernate. Fe is precipitated from strong KOH solution. K and residual Cu are separated by ion exchange.

Recovery: 80+%

Time Required: 6 Hours

Step 1 - Zn target, approximately 5 g., is dissolved in a minimum of HCl. Solution is diluted to 100 ml.

Step 2 - 20 mg. each of Fe (III) and Cu (II) carriers are added.

Step 3 - pH is adjusted to 5.5 with NH_4OH; solution allowed to digest 15 minutes.

Step 4 - Precipitate is removed by centrifugation and dissolved in HCl. A second precipitation is performed to insure separation from Cu.

Step 5 - Precipitate is dissolved in a minimum amount of HCl; volume is adjusted to 20 ml. with H_2O; an excess of KOH is added.

Step 6 - Heat to boil; precipitate is separated by centrifugation. Supernate, which contains activity as gallate ion, is reserved.

Step 7 - Precipitate is dissolved in HCl and a second precipitation is made.

Step 8 - Supernates are combined, neutralized with HCl and excess HCl is added to make solution 3N in HCl.

Step 9 - Solution is passed through a Dowex-1 column which has been conditioned with 3N HCl. Three column volumes of 3N HCl are passed through column to remove K and residual Cu. Ga is eluted with 0.2N HCl.

Step 10 - Solution is evaporated to near dryness; organic matter is removed by evaporation with HNO_3. Repeated evaporations with HCl convert the gallium to the chloride.

Procedure 5

Gallium

Source: H. J. M. Bowen, Internat. J. of Applied Radiation and Isotopes 5, 227 (1959).

Target Material: 0.3 g. tomato seeds; 5 g. blood.

Irradiation Time: 12 hours at approximately 1×10^{12} n/cm^2/sec.

Time Required: (Mo + Ga) approximately 4 hours for 8 samples.

Step 1 - Seeds are dissolved in hot fuming HNO_3. Blood is dissolved in hot fuming HNO_3 plus a few drops perchloric acid.

Step 2 - Carriers: 10 mg. Mo as ammonium molybdate; 5 mg. Ga as gallium nitrate. Holdback carriers: Cu, Co, Mn, P and Y.

Step 3 - Solution is evaporated to approximately 1 ml. Made up to 10 ml. and 6N in HCl.

Step 4 - Solution is transferred to separatory funnel and shaken with equal volume of ether; aqueous layer is discarded; ether is washed twice with 6N HCl.

Step 5 - Ether layer is extracted twice with 5 ml. H_2O. Aqueous layers are combined and boiled to remove ether.

Step 6 - Aqueous fraction is made 2N in HCl and MoS is precipitated with ammonium sulfide.

Step 7 - Supernate (containing Ga) is boiled to remove H_2S and made alkaline with potash and scavenged three to four times with $Fe(OH)_3$.

Step 8 - Gallium is precipitated as 8-hydroxyquinolate in an ammonium acetate buffer solution of pH-6.

Chemical Yield: 50-70%. Chief contaminant in gallium fraction identified as P^{32}.

Procedure 6

Gallium

Source: W. A. Brooksbank, G. W. Leddicotte and H. A. Mahlman, Anal. Chem. Div., Oak Ridge National Laboratory, Oak Ridge, Tennessee, J. Phys. Chem. 57, 815 (November 1953).

Gallium in Aluminum

Target: 0.1 to 0.2 g. aluminum in quartz tubes.

Step 1 - Aluminum target is dissolved in small amount of concentrated HCl. Standardized Ga carrier and concentrated HBr are added and the solution is evaporated to dryness.

Step 2 - Residue is dissolved in 6N HCl and solution is extracted three times with equal volume of diethyl ether.

Step 3 - Extracts are combined and washed with 6N HCl and the gallium is back extracted into an equal volume of H_2O. Cu, Fe and Ba holdback carriers are added to the solution.

Step 4 - Cu is removed by H_2S precipitation; Fe and Ba are removed by precipitation with NaOH and Na_2CO_3.

Step 5 - After filtration, solution is made 6N in HCl and the gallium is extracted with an equal volume of diethyl ether.

Step 6 - Gallium is back extracted into H_2O and the aqueous layer is heated to expel equilibrated ether.

Step 7 - A few ml. of 8-hydroxyquinoline solution (50 g./l in 2<u>M</u> acetic acid) are added and gallium 8-hydroxyquinolate is precipitated with dropwise addition of 6<u>M</u> ammonium acetate.

Step 8 - After filtration, precipitate is washed with H_2O, dried for 15 minutes at 110°C, weighed; counted with scintillation detector.

Procedure 7

Aluminum

Source: R. A. Rightmire, T. P. Kohman and A. J. Allen, Internat. J. Applied Radiation and Isotopes <u>2</u>, 274 (1957).

Element: Al - Carrier-free Al^{26}.

Separated from: Magnesium (α bombarded).

Decontamination Factor: $>10^8$

Chemicals and Equipment: Polyethylene ion exchange columns as follows:

2 - 35 cm. x 1 cm.
1 - 60 cm. x 1 cm.
Dowex-1 (100-200 mesh) - prepared by washing with 12<u>N</u> HCl, followed by H_2O.
Dowex-50 (50-100 mesh) - prepared by washing thoroughly with 6N HCl until free of iron, then with H_2O.
Glassware - coated with a thin silicone film.

Freshly distilled H_2O and freshly prepared NH_4OH were used throughout.

Step 1 - Dissolve activity from magnesium target with 6N HCl.

A. Separation of Al from Mg and Na

Step 2 - Add H_2O until solution volume is approximately twice the amount of 6N HCl added in Step 1. Add 10 mg. each of Be^{+2}, Ca^{+2} and Sc^{+3} carriers plus methyl red indicator. Add NH_4OH to methyl red end point to precipitate $Be(OH)_2$ and $Sc(OH)_3$. Digest at 50-60°C for 10 minutes and cool.

Step 3 - Centrifuge; wash precipitate with 0.001N NH_4OH.

B. Purification of Al^{26}

Step 4 - The precipitate is dissolved in 100 ml. of 0.15N HCl + 0.1M $H_2C_2O_4$ and introduced onto a small anion exchange column which had been filled to a height of 20 cm. and washed with 500 ml. of (0.12N HCl + 0.1M $H_2C_2O_4$). See Note 1.

Step 5 - The Be^{2+} is eluted with 50 ml. of (0.15M HCl + 0.1M $H_2C_2O_4$), or until no precipitate of $Be(OH)_2$ forms in the elute upon addition of NH_4OH.

Step 6 - The Al^{3+} is eluted with 50 ml. of 12N HCl, and the eluate is diluted with 100 ml. H_2O and 30 mg. Fe^{3+} is added.

Step 7 - The solution is made slightly basic with NH_4OH, and the precipitate is digested at 50-60°C for one half to one hour.

Step 8 - The precipitate is centrifuged and washed, and the supernatant solution and washings discarded.

Step 9 - The precipitate is dissolved with 50 ml. 0.50N HCl and the solution introduced onto a small cation exchange column which had been filled to a height to 20 cm. and washed thoroughly with H_2O.

Step 10 - The flow rate is adjusted to 10 drops/minute and the column is washed with 50 ml. 0.80N HCl.

Step 11 - Fe^{3+} and Al^{3+} are eluted with a minimum of four column volumes 5N HCl.

Step 12 - Concentrated HNO_3 in a volume equal to the above is added, and the solution concentrated to one half volume by heating at 70-80°C. See Note 2.

Step 13 - Vanadium carrier solution is prepared by dissolving 10 mg. V_2O_5 in 5 ml. 12N HCl, and is added to the above solution.

Step 14 - The solution is made basic with a slight excess of dilute NH_4OH, and the precipitate centrifuged and washed with H_2O.

Step 15 - The precipitate is dissolved in 10 ml. 12N HCl, and the solution saturated with HCl gas. The solution is introduced onto a large anion-exchanger column which had been prepared by filling to a height of 50 cm. and washing with 12N HCl.

Step 16 - The flow rate is adjusted to 10 drops/minute, and the carrier-free Al^{26} is washed out with 1.5 column volumes of 12N HCl. See Note 3.

NOTES

(1) The flow rate was adjusted to 8-10 drops/minute.

(2) Vanadium is converted to its highest oxidation state.

(3) To convert to a chloride solution, 200 ml. of conc. HNO_3 were added, and the solution evaporated to 10 ml. in a silicone-coated beaker. The evaporation must be done cautiously because of the significant vapor pressure of $AlCl_3$ at elevated temperatures.

Procedure 8

Gallium

Source: G. M. Iddings, University of California, Lawrence Radiation Laboratory, Livermore, California.

Purification: 10^9 atoms of Ga^{72} isolated from a 36-hour old solution of 2.6×10^{14} fissions showed no detectable foreign radionuclides when followed through eleven half-lives.

Yield: About 70%

Step 1 - To a 6<u>N</u> HCl solution of mixed activities in a 125 ml. Erlenmeyer flask, add 10 mg. Ga carrier and 1 mg. Te^{+4} carrier. Boil solution for 10 minutes. Final solution should be approximately 20 ml. (Note 1)

Step 2 - Cool and transfer solution to a 60 ml. cylindrical, open-top, separatory funnel (with stem detached immediately below the stopcock). Add 4 ml. conc. HCl to the 20 ml. of 6<u>N</u> HCl to make solution 7<u>N</u> in HCl. Add approximately 25 ml. isopropyl ether and extract the Ga into the ether by rapid stirring with a motor-driven glass rod stirrer (paddle) for two minutes. Record time of this separation of Zn^{72} from Ga^{72}.

Step 3 - Drain and discard aqueous layer. Wash organic layer with approximately 15 ml. of 7<u>N</u> HCl for two minutes. Repeat 7<u>N</u> HCl wash.

Step 4 - Back extract the Ga from the ether with approximately 15 ml. of water for two minutes. Repeat the back extraction with 10 ml. of water and combine water layers in a 40 ml. centrifuge cone.

Step 5 - Add 5 mg. Fe^{+3} carrier. Add 10<u>N</u> NaOH until pH is approximately 13 (0.1<u>N</u> in OH^-). Heat on boiling water bath 3 minutes to coagulate $Fe(OH)_3$ ppt.

Cool to room temperature. Centrifuge and discard the $Fe(OH)_3$ precipitate.

Step 6 - Transfer the supernate to a new 60 ml. cylindrical separatory funnel (identical with the one used previously). Add a measured amount (4 or 5 drops) of conc. formic acid until the pH is approximately 7. Then add twice this amount of conc. formic acid. (The solution is buffered at pH 3.3-3.6 by adding the formic acid.) Add 30 ml. of 0.40<u>M</u> TTA in benzene and extract the Ga into the TTA-benzene phase by rapid stirring for 15 minutes.

Step 7 - Drain and discard aqueous layer. Wash organic layer with approximately 15 ml. of 1<u>N</u> NaOH for ten seconds. Immediately drain aqueous layer and repeat 1<u>N</u> NaOH wash. Wash organic layer with approximately 15 ml. of water for ten seconds. Wash organic layer with approximately 15 ml. of 1<u>N</u> HCl twice. (Step 7 should be done quickly because Ga is slowly back extracting from the organic layer during these washes. See Note 2.)

Step 8 - Back extract the Ga with approximately 15 ml of conc. HCl for 20 minutes. Repeat conc. HCl back extraction for 20 minutes.

Step 9 - Combine conc. HCl solutions and dilute it with water until the solution is approximately 7<u>N</u> HCl (add approximately 21 ml. of water to 30 ml. of conc. HCl). Transfer 7N HCl solution to a 125 ml. cylindrical, open-top, separatory funnel (with stem detached immediately below the stopcock). Add approximately 30 ml. of isopropyl ether and extract the Ga into the ether by rapid stirring for two minutes.

Step 10 - Drain and discard aqueous layer. Wash organic layer with approximately 15 ml. of 7N HCl for two minutes. Repeat 7N HCl wash.

Step 11 - Back extract the Ga from the ether with approximately 10 ml. of water for two minutes. Repeat the back extraction with approximately 10 ml. of water.

Step 12 - Combine water solutions of Ga in a 40 ml. centrifuge cone. Add approximately 0.5 ml. of a saturated solution of NH_4Ac. Add NH_4OH dropwise until the solution is approximately pH-6. Heat in boiling water bath to precipitate $Ga(OH)_3$ for ten minutes.

Step 13 - Filter out $Ga(OH)_3$ with Whatman No. 42 filter paper. Wash precipitate with 2 per cent NH_4NO_3. Ignite filter paper in a poreclain crucible for one hour at 900-1000°C.

Step 14 - Powder the Ga_2O_3 and transfer it to a tared aluminum "hat". Weigh. Mount hat on aluminum counting plate and count the 14.3-hour Ga^{72} in a beta and/or gamma counter.

NOTES

(1) Boiling in 6N HCl reduces any Te^{+6} to Te^{+4} and ensures complete exchange between Te carrier and radioactive Te.

(2) The 1N NaOH washes the "free" TTA away from the benzene layer, leaving the Ga-TTA chelate. In subsequent washes with 1N HCl, the equilibrium is shifted so that the Ga tends to leave the organic layer. However, in low acid (1N HCl) the rate is slow (similar to Fe^{+3}, Al and Be). Elements such as Zr, Np^{+4}, rare earths, Pa, Th, etc., are rapidly back extracted into the 1N HCl when there is essentially no "free" TTA in the benzene.

Procedure 9

Gallium

Source: Harrison Brown and Edward Goldberg, Science 109, 347 (1949).

Target: Unknown - 0.3 to 0.5 g. iron meteorite.

Standard - 10 mg. gallium 8-hydroxyquinolate.

Irradiation - approximately 30 minutes at 10^{12} $n/cm^2/sec$.

A. Chemical Processing of Meteorite Unknown

Step 1 - Sample is dissolved in hot concentrated HCl in 50 ml. beaker. 4-5 mg. Ga^{+3} carrier added.

. Step 2 - Adjust solution to 5.5 to 6.5M in hydrochloric acid. Extract gallium with equal volume of HCl saturated ether. Strip gallium from ether phase with H_2O.

Step 3 - Repeat Step 2. Evaporate ether from aqueous phase.

Step 4 - Precipitate ferric ion by addition of NaOH (hydroxide concentration of 1-2M). Add one drop of aerosol, centrifuge, and discard precipitate. Acidify supernate to pH-1 and heat to 60-70°C.

Step 5 - Add 5 ml. of a 1 per cent acetic acid solution of 8-hydroxyquinoline. Add 3M ammonium acetate (dropwise) to completely precipitate gallium 8-hydroxyquinolate.

Step 6 - Filter; wash precipitate with hot water followed by ether. Dry sample 15 minutes at 110°C and determine yield.

B. Processing of Gallium Standard

Step 1 - Dissolve 10 mg. quantity of gallium 8-hydroxyquinolate, which was irradiated under identical conditions as the meteorite sample, in hot concentrated HCl.

Step 2 - Dilute to 50 ml. Take 0.5 ml. aliquot; add same quantity of gallium carrier as for the unknown and precipitate as above.

Procedure 10

Aluminum

Source: W. D. Ehmann and T. P. Kohman, Geochimica et Cosmochimica Acta 14, 340 (1958).

Materials: A. Chemicals - reagent grade

B. Filtering - analytical grades (Whatman)

C. Ion Exchange Resins

1. Dowex-1, X-10, 100-200 mesh anion exchange.
2. Dowex-50, X-8, 50-100 mesh cation exchange.

A. Procedure for Iron Meteorites

Iron meteorite sample--100 to 150 g. Washed with distilled H_2O and acetone.

Step 1 - Sample is dissolved in consecutive 200 ml. portions of aqua regia, each portion stirred in separate beakers until complete dissolution is achieved.

Step 2 - 25 ml. concentrated HNO_3 is added to combined solutions to oxidize all Fe^{2+} to Fe^{3+}. Solution is evaporated to near dryness with 500 ml. portions of HCl to remove excess HNO_3.

Step 3 - Solution is adjusted to one liter with 9M HCl (solution filtered [Whatman-50 paper] and residues discarded).

Step 4 - Accurately known quantities of the following carriers are added: Al^{+3}-20 mg.; Be^{2+}-13.9 mg.; Ca^{2+}-20 mg. Iron is removed by extraction into 9M HCl saturated isopropyl ether. Processing of the aqueous phase proceeds as follows:

Step 5 - The aqueous phase is adjusted to 10M in HCl (total volume approximately 750 ml.) and passed through a Dowex-1 column. Al^{3+}, which is not adsorbed in the column is retained in the elute along with Ni^{2+}, Ca^{+2}, Be^{2+} and others. Column is washed with 500 ml. of 10M HCl and the washings combined with the main elute.

Step 6 - The elute from Step 5 is reduced in volume to 300 ml. and $Al(OH)_3$ and $Be(OH)_2$ are precipitated with NH_4OH (pH approximately 7). Hydroxides are filtered on Millipore HA paper and washed with 25 ml. of 5% NH_4Cl adjusted to approximately pH 7. The hydroxides are dissolved in dilute HCl and reprecipitated and filtered twice.

Step 7 - $Al(OH)_3$ and $Be(OH)_2$ precipitates are transferred to a 250 ml. beaker, 10-20 mg. Fe^{3+} carrier is added plus 25 ml. of 8M NaOH. Heat to boiling and filter insoluble hydroxides scavenged by $Fe(OH)_3$ precipitated on fritted glass.

Step 8 - Reprecipitate $Al(OH)_3$ and $Be(OH)_2$ with 6M HCl after diluting filtrate to 250 ml. with H_2O. Dissolve precipitate in dilute HCl and reprecipitate twice with NH_4OH to remove Na^+.

Step 9 - Dissolve $Al(OH)_3$ and $Be(OH)_2$ in minimum volume of 6M HCl. Dilute to 50 ml. with H_2O and make to 1.1M HCl with 6M HCl.

Step 10 - Pass solution through 25 ml. resin volume Dowex-50 ion exchange column (10 in. x 1/2 in. diameter) at flow rate of approximately 1 ml./min. Elute Be^{2+} with 6-7 resin volumes of 1.1M HCl. Al^{3+} is held in column but will elute with 12 to 15 resin volumes of 1.1M HCl.

Step 11 - Elute Al^{3+} with 100 ml. of 3M HCl.

Step 12 - Reduce volume of Al^{3+} containing solution to 5 ml. on hot plate. Cool on ice bath to 10°C and add 5 ml. of 12M HCl. Bubble dry HCl gas through solution for 5 minutes; add 10 ml. ethyl ether and continue gassing until solution layers combine indicating saturation by HCl. $AlCl_3 \cdot 6H_2O$ precipitates on standing for extended period in ice bath. Filter precipitate by suction on fritted glass disc and wash with cold 1:1 12M HCl-ether solution saturated with HCl.

Step 13 - Dissolve $AlCl_3 \cdot 6H_2O$ in 5 ml. H_2O; reprecipitate twice and finally dissolve in distilled H_2O.

Step 14 - Precipitate $Al(OH)_3$ with NH_4OH at methyl-red end-point. Collect precipitate on Millipore HA filter in Büchner funnel.

Step 15 - Ignite to Al_2O_3 at 1000°C in platinum dish.

B. Procedure for Silicate Materials

Procedure is similar to that for meteorite sample except for dissolution of sample, amounts of reagents used and sizes of ion exchange columns.

REFERENCES

(1) Simanton, J. R., Rightmire, R. A., Long, A. L. and Kohman, T. P., Phys. Rev. 96, 1711 (1954).

(2) Rightmire, R. A., "Doctoral Dissertation," Carnegie Institute of Technology, U.S.A.E.C. Document NYO-6633 (1957).

(3) Rightmire, R. A., Kohman, T. P., J. Appl. Rad. Isotopes 2, 274 (1957).

(4) Kohman, T. P., Rightmire, R. A., Ehmann, W. D. and Simanton, J. R., "Radioisotopes in Scientific Research," Volume 1, Proc. 1st UNESCO Inst. Conf., Paris, 1957, Pergamon Press (1958).

(5) Foster, L. S., J. Am. Chem. Soc. 61, 3122 (1939).

(6) Foster, L. M. and Stumpf, H. C., J. Am. Chem. Soc. 73, 1590 (1951).

(7) Gooch, F. A. and Havens, F. S., Am. J. Sci. 2, 416 (1896).

(8) Goto, H., J. Chem. Soc. Japan 54, 725 (1933).

(9) Hopkins, B. S., "Chapters in the Chemistry of the Less Familiar Elements," Stripes Publishing Company, Champaign, Illinois (1939).

(10) Steinbach, J. F. and Freiser, H., Anal. Chem. 26, 375 (1954).

(11) Wold, A., Baird, J. H., and Hough, C. R., Anal. Chem. 26, 546 (1954).

(12) Bolomay, R. A. and Wish, L., J. Am. Chem. Soc. 72, 4483 (1958).

(13) Eshelman, H. C., Anal. Chem. 31, 183 (1959).

(14) Sandell, E. B., "Colorimetric Determination of Traces of Metals," 2nd Edition, Interscience Publishers, Inc., New York (1950).

(15) Luke, C. L. and Campbell, M. E., Anal. Chem. 28, 1340 (1956).

(16) Kambara, T. and Hoshitani, H., Anal. Chem. 31, 567 (1959).

(17) Moeller, T. and Cohen, A. J., Anal. Chem. 22, 686 (1950).

(18) Lecroix, S., Anal. Chim. Acta 1, 260 (1947). (In French)

(19) Meunier, P., Compt. rend. 199, 1250 (1934).

(20) Baudisch, O. and Furst, R., Ber. deut. chem. Ges. 50, 324 (1917).

(21) Chernikov, Y. A. and Kobkina, B. M., Zavodskaya Lab. 15, 1143 (1949).

(22) Milner, G. W. C., Wood, A. J. and Woodhood, J. L., Analyst 79, 272 (1954).

(23) Bock, R. and Herrman, M., Z. anorg. u. allgem. Chemie 284, 288 (1956).

(24) Swift, E. H., J. Am. Chem. Soc. 46, 2378 (1954).

(25) Nachtrieb, N. H. and Fryxell, R. E., J. Am. Chem. Soc. 71, 4035 (1949).

(26) Bennet, W. and Irvine, J. W., Mass. Inst. Technol. Lab. of Nuclear Sci. Prog. Rept., (February, 1953).

(27) Bock, R., Kusche, H. and Beck, E., Z. Anal. Chem. 138, 167 (1953).

(28) Kitahara, S., Bull. Inst. Phys. Chem. Research (Tokyo) 24, 454 (1948).

(29) Bock, R., Z. Anal. Chem. 133, 110 (1951).

(30) Johnson, S. E. J., "Colorimetric Determination of Traces of Metals," 2nd Edition, Interscience Publishers Inc., New York (1950).

(31) Sundaram, A. K. and Banerjaee, S., Anal. Chim. Acta 18, 526 (1953).

(32) White, J. C., Oak Ridge National Laboratory, Presented at Pittsburgh Conference on Anal. Chem. and Applied Spectroscopy, March 1957.

(33) Morrison, G. H. and Freiser, H., "Solvent Extraction in Analytical Chemistry," John Wiley and Sons, Inc., New York (1957).

(34) Klement, R. and Sandmann, H., Z. Anal. Chem. 145, 325 (1955).

(35) Strelow, F. W. E., Anal. Chem. 31, 1974 (1959).

(36) Kejima, S. and Kakihana, H., Japan Analyst 2, 421 (1953) and 3, 42 (1954).

(37) Kraus, K. A. and Nelson, F., "Symposium on Ion Exchange and Chromatography in Analytical Chemistry," A.S.T.M. Special Technical Publication No. 195 (January 1958).

(38) Kraus, K. A., Nelson, F. and Smith, G. W., J. Phys. Chem. 58, 11 (1954).

(39) Freund, H. and Miner, F. J., Anal. Chem. 25, 564 (1953).

(40) Horton, A. D. and Thomason, P. F., Anal. Chem. 28 1326 (1956).

(41) Kraus, K. A. and Nelson, F., Proceedings, Intern. Conf. on Peaceful Uses of Atomic Energy 7, pp. 113, 131, United Nations (1956).

(42) Paris, J. P., Anal. Chem. 32, 520 (1960).

(43) Marinsky, J. A. and Eichler, E., J. Inorg. and Nucl. Chem. 12, 223 (1960).

(44) Gruverman, I. J. and Kruger, P., J. Applied Radiation and Isotopes 5, 21 (1959).

(45) Hoffman, J. I., "Preparation of Pure Gallium," N.B.S. Research Paper R.P. 734.

(46) Lundell, W. F. et al., "Applied Inorganic Analysis," 2nd Edition, John Wiley and Sons, Inc., New York (1953).

(47) "Chemical Analysis of Aluminum," 3rd Edition, Alcoa Research Laboratories, New Kensington, Pennsylvania (1950).

(48) Dennis, L. M. and Bridgman, J. A., J. Am. Chem. Soc. 40, 1534 (1918).

(49) Guinn, V. P. and Wagner, C. D., Anal. Chem. 32, 317 (1960).

USAEC Office of Technical Information Extension, Oak Ridge, Tennessee