546.7
N669r
c.5

NAS-NS
3017

National
Academy
of
Sciences

National Research Council

NUCLEAR SCIENCE SERIES

The Radiochemistry of Iron

LOS ALAMOS NATIONAL LABORATORY
3 9338 00079 1219

U.S.
Atomic
Energy
Commission

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
Centre d'Etude de l'Energie Nucleaire
Mol-Donk, Belgium

JAMES DeVOE
University of Michigan

WILLIAM MARLOW
National Bureau of Standards

546.7
N669r
c.5

CHEMISTRY—RADIATION AND RADIOCHEMISTRY

The Radiochemistry of Iron

By J. M. NIELSEN

Hanford Laboratories
Hanford Atomic Products Operation
Richland, Washington

August 1960

LOS ALAMOS
SCIENTIFIC LABORATORY

FEB 15 1961

LIBRARIES
PROPERTY

LOS ALAMOS NATL. LAB. LIBS.
3 9338 00079 1219

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

CONTENTS

The Radiochemistry of Iron

By J. M. Nielsen
Hanford Laboratories
Hanford Atomic Products Operation
Richland, Washington
August 1960

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

"A Comprehensive Treatise on Inorganic and Theoretical Chemistry", J. W. Mellor, Vol. XII, XIII and XIV, Longmans, Green and Co., New York (1931).

"Ferrous Analysis. Modern Practice and Theory", E. C. Pigott, 2nd ed. Rev., pp. 215-231, John Wiley and Sons, Inc., New York (1953).

"The Chemical Elements and Their Compounds", N. V. Sidgwick, Vol. II, pp. 1322-1374, University Press, Oxford (1951).

"Treatise on Inorganic Chemistry", H. Remy, Vol. II, pp. 252-290, Elsevier Publishing Co., New York (1956).

"Analytical Chemistry of the Manhattan Project", C. J. Rodden and J. C. Warf, pp. 415-428, McGraw-Hill Book Co., New York (1950).

"Applied Inorganic Analysis", Hillebrand, Lundell, Bright and Hoffman, 2nd ed., John Wiley and Sons, Inc., New York (1953).

"Scott's Standard Methods of Chemical Analysis", N. H. Furman, Editor, 5th ed., Vol. I, "Iron", pp. 462-497, D. Van Nostrand Co., Inc., New York (1939).

II. REVIEWS OF THE RADIOCHEMISTRY OF IRON

"Radioactive Isotopes of Iron and Their Use in Chemistry and Biology", V. I. Goldanskii and M. B. Neiman, Uspekhi Khim. 19, 320-41 (1950) (In Russian).

"Iron-60", J. C. Roy and T. P. Kohman, Can. J. Phys. 35, 649-55 (1957).

III. TABLE OF ISOTOPES OF IRON

Isotope	Percent Abund.	Half Life	Decay	Energy (Mev)	Method of Preparation
Fe$^{52(1)}$		8.2 h	β^+(56.5%) EC(43.5%) γ ($\sim$100%)	0.804 0.165	Cr^{50}(α,2n)
Fe$^{53(1)}$		8.9 m	β^+ β^+ β^+(?) γ	2.84 2.38 1.57 0.38	Cr^{50}(α,n) Fe^{54}(n,2n)
Fe^{54}	5.84				
Fe^{55}		2.60 y	EC	0.22 (internal bremsstrahlung)	Fe^{54}(n,γ) Fe^{54}(d,p) Mn^{55}(p,n) Ni^{58}(n,α)
Fe^{56}	91.68				
Fe^{57}	2.17				
Fe^{58}	0.31				
Fe^{59}		45.1 d	β^-(46%) β^-(54%) β^-(0.3%) γ (2.8%) γ (57%) γ (43%)	0.271 0.462 1.560 0.191 1.098 1.289	Fe^{58}(n,γ) Co^{59}(n,p) Ni^{62}(n,α)
Fe^{60}		$\sim$3x10^5 y	β^-		Cu(400 Mev p)
Fe$^{61(2)}$		6.0 m	β^- γ	2.8 0.29	Ni^{64}(n,α) Ni^{64}(d,αp) Cu^{65}(n,αp)

Unless otherwise noted these data are from "Table of Isotopes" by D. Strominger, J. M. Hollander and G. T. Seaborg, Reviews of Modern Physics 30, No. 2, Part II, 628-629 (1958).

IV. REVIEW OF THOSE FEATURES OF IRON CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS

Iron is the fourth most abundant element in the crust of the earth of which it constitutes 5.1 percent. It is found in practically all rocks and soils and is present in hundreds of minerals. Because of its abundance and its metallurgical properties, it is the basic material of civilization. Compounds of iron are of fundamental importance to living organisms, both animal and vegetable, being required mainly to promote oxidation. Iron compounds are important catalysts for chemical reactions, especially oxidation-reduction reactions. Because of this importance and widespread abundance, iron analyses are perhaps the most commonly performed chemical analyses, and iron separation prior to other analyses is very important.

1. Metallic Iron and the Iron Oxides and Hydroxides

Iron is a white, lustrous, rather soft metal (hardness 4.5) with a specific gravity of 7.86 and a melting point of 1528°C. It exists in two fundamentally different crystalline forms depending upon the temperature. Below 906°C and above 1401°C it forms a body-centered cubic lattice. At temperatures below the Curie point (768°C) iron is known as α-iron and is ferromagnetic. Between 906°C and 1401°C the lattice is a face-centered cubic, non-magnetizable form known as γ-iron. The non-magnetic body-centered cubic lattice iron between 768 and 906°C is sometimes known as δ-iron.

Iron is generally produced by reduction of oxide or carbonate ores with carbon monoxide. This crude iron is only 92-96 percent pure. Steel is produced from crude iron by eliminating the major proportion of the impurities, controlling the amount of carbon, and adding alloying metals, especially manganese. Pure iron can be prepared (1) by heating chemically purified iron oxalate in the air to form the oxide which is subsequently reduced with hydrogen; (2) by thermally decomposing iron pentacarbonyl; or (3) by electrolyzing aqueous solutions of ferrous salts. The potential for the Fe-Fe(II) couple is + 0.440 volt at 25°C.

Iron dissolves in hydrochloric acid, dilute sulfuric acid and dilute phosphoric acid to yield ferrous salts of these acids. Nitric, perchloric, chloric, bromic and iodic acids, although possessing definite oxidizing properties, also yield ferrous salts if the acids are dilute and the reaction progresses at room temperature. With concentrated or heated acids ferric salts are formed. Hydrofluoric acid yields slightly soluble ferrous fluoride. Concentrated nitric, iodic and chloric acids dissolve iron very slowly, probably because of the formation of insoluble oxide films. Nitric acid with a specific gravity of 1.2 dissolves iron more rapidly than any other concentration of nitric acid. Iron is not dissolved by cold, concentrated sulfuric acid but does dissolve in the hot acid with the evolution of sulfur dioxide to form ferric sulfate. Iron dissolves rapidly in aqueous solutions of sodium hypochlorite, ammonium persulfate, and copper ammonium chloride,

Iron forms the oxides FeO, Fe_2O_3, Fe_3O_4 and probably unstable FeO_2, Fe_2O_5 and an iron peroxide or peroxyhydrate, and the hydroxides $Fe(OH)_2$ and $FeO(OH)$. Fe_3O_4 is a double compound (spinel) of FeO and Fe_2O_3. Fe_2O_3 has a decomposition temperature of 1300°C and the other oxides are converted to it by heating below this temperature in the presence of oxygen. Ignition of Fe_2O_3 at 1000-1100°C is recommended for analytical purposes. Heating above 1400°C converts Fe_2O_3 to Fe_3O_4 and finally to FeO by the loss of oxygen. Strongly ignited Fe_2O_3 dissolves with difficulty in hot hydrochloric acid, being more readily soluble in hot 8:3 sulfuric acid. The oxides are also readily attacked by hydrofluoric acid. The unignited oxides are soluble in hot hydrochloric acid. Their rate of solution may be increased by adding reducing agents such as stannous chloride.

Ferrous hydroxide, $Fe(OH)_2$, is a white flocculent material precipitated by alkaline hydroxides from solutions of ferrous salts in oxygen-free solution. It has a solubility product of 3×10^{-14}. In the presence of oxygen (or air) the hydroxide is slowly oxidized to the ferric oxide hydrate, with a color change through green and black to deep red brown. Ammonium hydroxide does not completely precipitate ferrous hydroxide, indeed, $Fe(OH)_2$ is not precipitated in the presence of a high concentration of ammonium salts. $Fe(OH)_2$ is soluble in acids and in concentrated sodium hydroxide. The only known hydrated oxide of ferric iron has the composition $Fe_2O_3 \cdot H_2O$ or FeO(OH). It is formed as an amorphous, red-brown precipitate from ferric salt solution by hydrolysis or addition of alkali or ammonia, and has a solubility product of 10^{-36}. The precipitate has a high surface activity and on standing forms a gel. Freshly precipitated ferric oxide hydrate is readily soluble in dilut strong acids and is slightly soluble in hot concentrated alkali hydroxide solutions.

2. Soluble Compounds of Iron

In most of the compounds of interest to radiochemists, iron has the oxid tion state of +2(ferrous) or +3(ferric). In general, the ferrous and ferric salts have similar solubilities in water. The nitrates, sulfates, chlorides, bromides, thiocyanates and lactates are generally insoluble. Most ferrous salts are not completely stable in air. They are fairly stable in the presen of air when in acid solution, but readily oxidize when the solutions are basi Ferrous iron is quantitatively oxidized to the ferric state by strong oxidizing agents such as nitric acid, hydrogen peroxide, dichromate, permanganate and ceric sulfate. Ferric iron is quantitatively reduced to the ferrous stat by reducing agents such as stannous chloride, hydroxylamine hydrochloride, hydroquinone, zinc and hydrochloric acid, metallic mercury, iron and hydrogen sulfide. Iron may exhibit oxidation states of +3, +4 and +6 in the ferrite (FeO_2^-), perferrite ($FeO_3^=$) and ferrate ($FeO_4^=$) compounds. These salts are generally rather unstable. Iron also forms numerous nitrosyl and carbonyl compounds.

3. Insoluble Compounds of Iron

Some of the insoluble compounds of iron are listed in Table II.

Although most analytical procedures for iron are volumetric, some gravimetric procedures are used and certain precipitation reactions are useful in analyses. Of these, some discussion follows for the ferric oxide hydrate, sulfide, basic formate, periodate and cupferrate precipitates, and the salt of N-benzoylphenylhydroxylamine. A gravimetric method may be especially valu able when several elements must be separated in sequence from one sample.

TABLE II

Compound	Solubility in Water g/100 ml (25°C)
$FeOH(C_2H_3O_2)_2$ (basic acetate)	i.
$Fe_3(AsO_4)_2 \cdot 6H_2O$	i.
$FeAsO_4 \cdot 2H_2O$	i.
$Fe(C_7H_5O_2)_3$ (benzoate)	i.
$FeCO_3$	0.072 (18°C)
$Fe\left[C_6H_5N(NO)O\right]_3$ (cupferrate)	$2x10^{-6}$ (18°C)
$Fe_3\left[Fe(CN)_6\right]_2$	i.
$Fe_2Fe(CN)_6$	i.
$Fe_4\left[Fe(CN)_6\right]_3$	i.
$Fe_3(OH)_2(HCOO)_7 \cdot 4H_2O$ (basic formate)	6.1
FeF_3	5.59
$FeO(OH)$ (oxide hydrate)	$2.6x10^{-9}$
$Fe(OH)_2$	0.00067
FeO	i.
Fe_3O_4	i.
Fe_2O_3	i.
$FeC_2O_4 \cdot 2H_2O$ (oxalate)	$7.75x10^{-3}$
$Fe_3(PO_4)_2 \cdot 8H_2O$	i.
$FePO_4 \cdot 2H_2O$	v.sl.s.
$Fe_4(P_2O_7)_3 \cdot 9H_2O$	i.
FeS	0.00062 (18°C)
Fe_3S_4	i.
FeS_2	0.00049
$FeSO_3 \cdot 3H_2O$	v.sl.s.
$Fe(VO_3)_3$	i.

Ferric oxide hydrate: Precipitation of iron as the ferric oxide hydrate [FeO(OH)] is accomplished in a NH_4OH and NH_4Cl buffered solution. This reaction is useful in separating iron from the alkalis, alkaline earths, zinc, lead, cadmium and other metals whose hydroxides are precipitated at higher pH's than iron, or which can be held in solution by excess ammonium chloride. Organic oxyacids, alcohols, sugars, pyrophosphate, arsenate or arsenite inhibit or retard this precipitation. Ammonium hydroxide also precipitates aluminum, trivalent chromium, titanium, zirconium, phosphates, arsenates, and some vanadium and molybdenum under the conditions employed to precipitate iron. Ferric oxide hydrate is a non-specific, non-isotopic carrier having high surface activity which especially occludes ions of copper, nickel, cobalt and manganese and which adsorbs foreign ions even after the precipitate is formed. This makes it useful as a scavenger but limits the application of this precipitate in radiochemical determinations of iron. (In at least one application, the adsorptive properties of this precipitate were of analytical value in an iron determination. A carrier-free isolation of Fe^{59} was made by J. D. Gile et al(3) where carrier-free Fe^{59} was quantitatively retained on filter paper as the radiocolloid. See Procedure 10, Section VII of this report.) Ferric oxide hydrate may be converted to Fe_2O_3 for weighing by heating in the presence of air to constant weight at 1000-1100°C.

Alkali hydroxides and peroxides completely precipitate ferric oxide hydrate in the absence of organic materials but do not effect as efficient a separation as NH_4OH from those metals such as cobalt, nickel and zinc which form ammonium complexes. Alkali carbonate solutions precipitate a basic ferric carbonate which can be hydrolyzed to the hydrated ferric oxide by boiling.

Ferrous sulfide: Ferrous sulfide can be precipitated from neutral or slightly acid solutions of either ferrous or ferric salts by ammonium sulfide, but a more easily filtered precipitate is obtained if the iron is reduced to the ferrous state first. Stokes and Cain(4) recommend the addition of some cadmium as collector. Prior removal of heavy metals by hydrogen sulfide precipitation in acidic solution is best avoided, since some metal sulfides, for example tin sulfide, carry down iron. A clean separation of iron as the sulfide is limited to samples which are free from metals that give only slightly soluble sulfides in excess ammonium sulfide. The most useful procedure is to precipitate the iron as the sulfide from an ammoniacal solution with the iron held in solution as a citrate or tartrate complex. If the solution contains sufficient tartrate, separation is obtained from aluminum, chromium, titanium, zirconium, niobium, vanadium, uranium and phosphate. Cobalt, copper, zinc and nickel are not separated. The ferrous sulfide precipitate is unstable and in the presence of air is oxidized to ferrous sulfate and finally to a brown basic sulfate. The fresh precipitate is usually dissolved in hydrochloric acid, oxidized to the ferric state by permanganate, precipitated as the hydrated oxide, muffled, and weighed.

Ferric basic formate: Willard(5,6) recommends the homogeneous precipitation of iron as the basic formate by urea hydrolysis, precipitating the main portion of the iron (over 90 percent) at a low pH (1.8) and the remainder at a pH of 3 to obtain quantitative precipitation and good separation from other metals (except aluminum). The precipitate formed is about 20 times smaller in volume than hydrous ferric oxide, easy to wash and filter, and does not readily adsorb metal impurities. This precipitation was recommended for the separation of iron from bivalent metals. The basic formate can be converted to the oxide for weighing by igniting at 1000-1100°C.

Ferric periodate: In the presence of aluminum a satisfactory separation of iron is not possible with the basic formate procedure. Ginsburg, Millar and Gordon(7) have shown that an effective separation of iron from aluminum can be obtained by a homogeneous precipitation of ferric periodate in a two stage precipitation from dilute nitric acid. The precipitate is dense, easily filtered and washed, and can be quantitatively converted to ferric oxide by careful ignition at 1000-1100°C to prevent spattering. By a single precipitation 85 mg iron was separated from 10 mg Al. By adding a second precipitation iron was separated from as much as 100 mg Al. Separation was not achieved from titanium, hafnium, zirconium, zinc or copper.

Ferric cupferrate: A cold 6 percent aqueous solution of cupferron (the ammonium salt of N-nitroso-N-phenylhydroxylamine) is commonly used to precipitate ferric iron from a dilute sulfuric or hydrochloric acid medium to effect its separation from aluminum, beryllium, chromium, cobalt, phosphorus, nickel, manganese, molybdenum, copper, zinc, vanadium, selenium, tellurium, boron and sexivalent uranium before other procedures are applied. This precipitant also gives quantitative precipitation of iron in the presence of organic material and large quantities of calcium and phosphate and is therefore useful for determining iron in biological materials(8). Lead, silver, mercury, bismuth, cerium, titanium, zirconium, thorium and tungsten are interfering elements. Cupferron cannot be used for the quantitative precipitation of less than milligram amounts of iron. The ferric cupferrate precipitate is not sufficiently stable to be weighed as such and it may contain some of the precipitant, but it can be converted to ferric oxide by washing while on the filter with hot ammonium hydroxide (this also dissolves the copper cupferrate that may have been carried and thus effects a separation from copper) or it can be directly ignited to the oxide at 1000-1100°C if care is used in the early stages of ignition. Ferric cupferrate is soluble in chloroform, carbon tetrachloride, diethyl ether and amyl acetate.

Ferric salt of N-benzoylphenylhydroxylamine: N-benzoylphenylhydroxylamine has been suggested(9) as an iron reagent similar to but more stable than cupferron. The ferric salt of this reagent can be weighed as such after drying at 110°C, an advantage in analyzing small quantities of iron by weight since the salt weighs about nine times as much as ferric oxide. This method is not as selective as the cupferron method in separating iron from aluminum, chromium and phosphate. Cobalt, cadmium, lead, mercury, manganese, nickel, uranium and zinc do not interfere.

4. Complex Ions of Iron

Iron readily forms a large number of stable complex ions in both of its common valence states. The tendency to form complex ions is particularly strong for the salts of iron with weak acid anions. Many iron compounds are capable of forming complex ions by adding ammonia; thus ferrous and ferric chlorides, in the dry state, both combine with six molecules of ammonia. These complexes undergo decomposition in water, but the ferrous ammoniates can be crystallized from solutions containing high concentrations of ammonium salts by saturation with ammonia. The cyanide complexes of iron are especially numerous and many of them are so stable that the complex salts can be readily obtained pure although it is not possible to isolate in the pure state the uncomplexed salts from which they are formed.

Ferric salts have a much stronger tendency to form complexes than the ferrous salts. Some of the few ferric salts which are not complex are those of strong acids such as perchloric, nitric, sulfuric and benzene-sulfonic. Ferrous iron forms complexes with alcohols, esters, diketones and aldehydes. Ferric iron forms similar complexes more readily and also forms complexes with ethers and phenols. Many of the resulting complexes with the organic compounds are colored and some of these colored compounds are useful in analysis. Since these complexes are often more stable in solution than the ammonia complexes, their presence inhibits the precipitation of iron as the hydroxide using ammonium hydroxide.

Irving and Williams(10,11) found that for divalent ions of the first transition metal series the order of stability of predominantly covalent complexes is $Zn > Cu > Ni > Co > Fe > Mn$ for many ligands. Calvin and Melchior(12) found a correlation between the stability of the chelates and the second ionization potentials for many metals in this series. Mellor and Maley(13,14) have pointed out that the stability of complexes of bivalent ions follows the order $Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg$ for many ligands, and that as a first approximation the stability seemed to decrease with increasing basicity of the metal. Although these two series are not in complete agreement, they show that the ferrous complexes are one of the least stable of this group of metals, a property made use of in many of the analytical separations methods. Tables of the stability constants for metal complexes with organic ligands(15) have been compiled from publications prior to January 1, 1956 and for inorganic ligands(16) prior to July 1957.

No attempt will be made to review the extensive but unsummarized literature pertaining to the complex ions of iron, but rather mention will be made of some of those complex ions of particular interest to the radiochemist in precipitation, solvent extraction and ion exchange applications.

Ferrous iron forms complexes with fluoride and chloride but not with bromide or iodide. The fluorides have the formulas, $M(FeF_3)$ and $M_2(FeF_4)$. The presence of fluoride ion in acid solutions of ferrous iron tends to increase the air oxidation of the iron. Three types of complex ferrous chlorides are known with the formulas, $M(FeCl_3)$, $M_2(FeCl_4)$ and $M_4(FeCl_6)$. Ferric iron forms complexes with fluoride, chloride and bromide with the stability decreasing in that order. No complex iodides are formed. The fluoride complexes of ferric ion have the formulas, $M(FeF_4)$, $M_2(FeF_5)$ and $M_3(FeF_6)$. The ferric chloride complexes have the formulas, $M(FeCl_4)$, $M_2(FeCl_5)$, $M_3(FeCl_6)$ and $M_4(FeCl_7)$. In hydrochloric acid solution an equilibrium exists between the ferric chloroanions present. At least one of these acids can be solvated by ethyl ether or iospropyl ether, which makes possible the solvent extraction of the solvated $HFeCl_4$ from concentrated hydrochloric acid solutions into these ethers. Ketones extract chloroferric acid more effectively than do the ethers. Most of the ion-exchange separations of iron are based on the differential exchange adsorption of these chloroanions on anion exchange resins.

Fluoride and pyrophosphate, and to a somewhat less extent metaphosphate, oxalate, tartrate and citrate, form such stable complexes with ferric ion that it is impossible to use many other complexing agents in the presence of these ions in acid media. Such strong complexes do not form with ferrous iron. The interference from the pyro- and metaphosphate complexes can be reduced by adding aluminum nitrate(17).

5. Chelate Compounds of Iron

Both ferrous and ferric iron readily form chelate compounds, many of which are important in the analytical and radiochemistry of iron. The stability constants of some of these chelate complexes are given in Table III. In other sections of this report the use of chelating agents in gravimetric analysis, solvent extraction and various chromatographic separations is discussed. In these methods use is made of the selectivity resulting from the large dependence of the stability constant of a given metal complex on the metal ion, and on the structure and arrangement of the functional groups on the chelating agent. Another property of many of the chelating agents which

TABLE III

Stability Constants for Some Chelate of Iron

Chelating Agent	Iron Ion	Stability Constant (log K)	Temp. °C	Ionic Strength (M)	Reference
Oxalic acid	Fe^{+2}	4.7	18	0	a
Oxalic acid	Fe^{+3}	9.4	--	0	b
Tartaric acid	Fe^{+3}	18.06?	--	--	c
2,2'-diaminodiethylamine	Fe^{+2}	6.23	30	1	d
Ethylenediamine	Fe^{+2}	4.28	30	1	e
Glycine	Fe^{+2}	4.3	20	0.01	f
Cysteine	Fe^{+2}	6.2	25	0.01	g
Acetylacetone	Fe^{+2}	5.07	30	0	h
Acetylacetone	Fe^{+3}	11.4	25	0	i
Glutamic acid	Fe^{+2}	4.6	20	0.01	h
Citric acid	Fe^{+3}	25.0	24	0.1	j
Ethylenediamine-NN-diacetic acid	Fe^{+2}	9.81	20	0.1	k
Ethylenediamine-NN-diacetic acid	Fe^{+3}	16.92	20	0.1	l
o-Hydroxyacetophenone	Fe^{+3}	10.52	25	3	m
8-Hydroxyquinoline	Fe^{+2}	8.0	20	0.01	n
8-Hydroxyquinoline	Fe^{+3}	14.52	25	0	o
Thenoyltrifluoroacetone	Fe^{+3}	6.9	25	0.1	p

TABLE III (CONTINUED)

Chelating Agent	Iron Ion	Stability Constant (log K)	Temp. ^{o}C	Ionic Strength (M)	Reference
2,2'-Dipyridyl	Fe^{+2}	4.36	25	0	q
EDTA	Fe^{+2}	14.2	20	0.1	r
EDTA	Fe^{+3}	25.7	25	1	s
1,10-Phenanthroline	Fe^{+2}	4.96	25	0.625 H_2SO_4	t

a. R. W. Money and C. W. Davies, Trans. Farad. Soc., 28, 609 (1932).

b. J. Lambling, Bull. Soc. Chim. France, 495 (1949).

c. V. F. Toropova, J. Gen. Chem. U.S.S.R., 15, 603 (1945).

d. H. B. Jonassen, G. G. Hurst, R. B. LaBlanc and A. W. Meibohm, J. Phys. Chem., 56, 16 (1952).

e. J. Bjerrum, "Metal-Amine Formation", P. Haase and Son, Copenhagen (1941).

f. A. Albert, Rev. Pure Appl. Chem., 1 (2), 51 (1951).

g. A. Albert, Biochem. J., 50, 690 (1952).

h. R. M. Izatt, W. C. Fernelius and B. P. Block, J. Phys. Chem., 59, 80 (1955).

i. J. Badoz-Lambling, Ann. Chim. (France), 8, 586 (1953).

j. R. C. Warner and I. Weber, J. Am. Chem. Soc., 75, 5086 (1953).

k. G. Schwarzenbach, G. Anderegg, W. Schneider and H. Senn, Helv. Chim. Acta, 38, 1147 (1955).

l. G. Anderegg and G. Schwarzenbach, Helv. Chim. Acta, 38, 1940 (1955).

m. A. Ågren, Acta Chem. Scand., 9, 39 (1955).

n. A. Albert, Biochem. J., 54, 646 (1953).

o. E. B. Sandell and D. C. Spindler, J. Am. Chem. Soc., 71, 3806 (1949).

p. A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", p 555 Prentice-Hall Inc., New York (1953).

q. P. Krumholz, J. Am. Chem. Soc., 71, 3654 (1945).

r. G. Schwarzenbach and E. Freitag, Helv. Chim. Acta, 34, 1503 (1951).

s. I. M. Kolthoff and C. Auerbach, J. Am. Chem. Soc., 74, 1452 (1952).

t. I. M. Kolthoff, D. L. Leussing and T. S. Lee, J. Am. Chem. Soc., 72, 2173 (1948).

is of value in analytical chemistry is the characteristic color obtained when the metal chelate is formed. Thus, for trace amounts of iron (less than 1 percent) colorimetric methods utilizing chelating agents and ferrous iron are generally used. The most common of these are the 2,2'-bipyridyl(18) and the 1,10-phenanthroline(19) methods which can be used for determinations of iron at concentrations as low as 0.1 ppm. For iron below this value some other colorimetric reagents such as 4,7-diphenyl-1, 10-phenanthroline (bathophenanthroline) and 2,4,6-tripyridyl-s-triazine are available for the determination of iron down to the few parts per billion range(20).

Both ferrous and ferric iron form chelate complexes with oxalate and tartrate which are important in determinations of iron. The ferrous oxalate complexes have the formula $M_2Fe(C_2O_4)_2$ and are less stable than the ferric oxalate complexes. Ferric ion forms dioxalate complexes, $MFe(C_2O_4)_2$, and trioxalate complexes, $M_3Fe(C_2O_4)_3$, the latter of whicn is more stable. The tendency to form these complexes is so great that calcium oxalate will dissolve in ferric chloride solution. Complex salts with tartrate(21) and citrate ions are also formed. An example of the application of these compounds is the use of citrate ion with biological samples to complex iron and keep it from precipitating with the aluminum phosphate(22).

6. Solvent Extraction

Solvent extraction is widely studied and applied in the radiochemistry of iron as well as in conventional iron analysis. Many solvents, complexing agents, and chelating agents are important.

Extraction of Iron Chloro- and Bromo-complexes: The extraction of ferric iron from hydrochloric acid solutions by organic solvents has been extensively studied since Rothe(23) discovered the extractability of iron from strong hydrochloric acid solutions into ethyl ether. Ether extraction methods are well suited to large quantities of iron but are not so well suited for trace quantities since the extraction coefficient is greater at high iron concentrations. Irvine is reported(24) to have found that radioiron extraction by ethyl ether from hydrochloric acid solutions in the range of 10^{-3} to 10^{-1} M ferric iron increases with increasing iron concentration and below 10^{-4} M iron the distribution ratio becomes constant. The amount of iron extracted also depends on the acid concentration and passes through a maximum at 6 N HCl. Isopropyl ether provides a more quantitative extraction than does ethyl ether, and is less sensitive to acid concentration at its maximum(25). Iron is best extracted with isopropyl ether from a solution 7.5 - 8.0 N in hydrochloric acid. With a solution containing 1 mg iron, 96 percent extraction is obtained with isopropyl ether compared to 80 percent with ethyl ether. Ferric iron is extracted from hydrochloric acid solutions by organic solvents as solvated $(H^+FeCl_4^-)_n$. With isopropyl ether n varies from 2 to 4 depending on the iron concentration(26,27). Ferrous iron is not extracted by ethyl ether from 6 N HCl where 99 percent ferric iron is extracted. Ether extraction from 6 N HCl solution provides satisfactory separation of Fe from Cu, Co, Mn, Ni, Al, Cr, Zn, V(IV), Ti and sulfate, but not from V(V), Sb(V), Ga(III), Te(III), Mo and phosphate. In some cases two ethereal layers are formed above the aqueous layer complicating the extraction.

The efficiency of extraction of iron is reduced by replacing the hydrochloric acid with hydrobromic acid and the acid concentration for maximum extraction is lowered(28). A maximum of about 73 percent is extracted with ethyl ether at a concentration of 4.7 N HBr compared with about 99 percent from 6 N HCl with ethyl ether(25) and 99.8 percent from 7.5 N HCl with isopropyl ether(26,29). Bock and Bock(30) found that only 0.1 percent of ferric iron is extracted by ether from 8 N nitric acid solutions at room temperature.

Esters and ketones have also been used as extractants for ferric iron from hydrochloric acid solutions. Amyl acetate is reported(31) to effect a separation of ferric iron from molybdenum and tin, but not from vanadium. Ketones extract chloroferric acid more effectively than do ethers or esters. The extraction coefficient of dilute ferric iron between isobutyl methyl ketone and 5.5 - 7 N HCl is 1000(32).

Thiocyanate extraction: Ferric iron forms red thiocyanate complexes which are extensively used for colorimetric analysis. In the presence of excess thiocyanate, the iron thiocyanate complex can be extracted into alcohols, ethers and esters. This system has been studied by Fischer and Bock(33) who report that 52 percent of the iron thiocyanate can be extracted from 0.5 N HCl with ethyl ether. The extraction into tributylphosphate at a pH greater than 1 is reported to provide a separation from Mo, Sb, U and Sn(31). This extraction is the basis for Procedure 13, Section VII of this report.

Diketone extraction: The 1:3 diketones are important in solvent extraction of iron because of their selectivity and their ready solubility in organic solvents. The simplest and one of the most studied of these is acetylacetone(34,35). Acetylacetonates of most metals are more soluble in organic solvents than other chelates used in analysis and this makes it possible to handle relatively large amounts of iron. It is also very effective for trace quantities as is illustrated by the work of Kenny et al(36) in which radioiron acetylacetonate was quantitatively extracted from neutron irradiated cobalt with xylene at pH 4-7 in less than spectrographic limits to give carrier-free Fe^{59}. In addition to xylene, carbon tetrachloride(37) and chloroform(38) are used. Cu, Mn, Mo, Ti, V, Zr, Be and Ga also extract under some conditions.

A number of substituted acetylacetonates have been studied, from which Reid and Calvin(39) selected 2-thenoyltrifluoroacetone (TTA) as having the most suitable characteristics of solvent stability, increased acid strength in the enol form, and stability toward oxidizing, reducing and hydrolyzing conditions. The extraction coefficient for ferric iron in a TTA-benzene system has been shown to be $\gg 1$(40) which is larger than for most trivalent metal ions (e.g. Al, Sc, Y, La, Ac, Bi. Tl(III) and Am(III)) and orders of magnitude larger for all the ions noted except Sc(41). This makes many separations possible by appropriate adjustment of pH. A study of the extraction of iron with TTA as a function of pH was reported by Cefola and Miccioli(42). TTA extraction curves are reported by Sheperd and Meinke(43). TTA permits extraction of iron at lower pH than acetylacetone, but the equilibrium is attained very slowly. The rate may be increased by increasing the TTA concentration or raising the pH. A summary of these factors is given by Moore(44). An important property of metal-TTA chelate compounds for use in radioisotope assay procedures is the ease with which they can be destroyed by heat on counting dishes, leaving no charred organic residue to complicate the counting. Procedures 1 and 2, Section VII of this report both use TTA extraction as a separations method.

Cupferron Extraction

Cupferron is not only an important selective precipitant for metals, but is also an effective agent for solvent extraction. Its use in extraction analysis was reviewed by Furman et al(45) whose theory was tested for ferric cupferrate by Sandell and Cummings(46). Cupferron extraction has been especially useful for samples containing organic material and large quantities of calcium and phosphate(8). Chloroform is generally used as the solvent(46,47,48), but ether(49), a mixture of ether and benzene(50), ethyl acetate(51) and other solvents are used. Cupferron extraction from 1 N mineral acid will remove not only iron, but Ga, Sb(III), Ti(IV), Sn(IV), Zr, V(V), U(IV), Mo(VI) and sometimes Cu(31). The extraction is quantitative from either hydrochloric or sulfuric acid solutions and is applicable to both micro and macro amounts.

Other Reagents

Some very sensitive iron reagents have been studied recently(20) whose use with iron radioisotopes has not yet been reported. The ferrous derivatives of these reagents have high solubility in organic solvents and are especially suitable for trace quantities which may make these reagents useful in iron radioisotope assay. Bathophenanthroline-iron chelates are usually extracted by isoamyl alcohol or n-hexyl alcohol from solutions at pH 4. Nitro-benzene is used for the tripyridyl-s-triazine-ferrous chelates from solutions at a pH of about 4 and perchlorate or iodide ions must be present. Isoamyl alcohol or chloroform is used for extracting the phenyl-2-pyridyl ketoxime-ferrous compound from 1 M sodium hydroxide solution.

Some other systems studied are the extraction of the citrate and tartrate-ferric iron complexes with tri-n-butyl amine(52), the extraction of the ferric 8-hydroxyquinolate with chloroform from acetic acid-acetate solution(36,38), the extraction of ferrous iron at a pH of 8-9 with a chloroform solution of isonitrosoacetophenone(53), extraction with various polyethers(54), and with tri-n-butyl phosphate(55).

7. Chromatographic Behavior of Iron

The chromatographic behavior of iron has been extensively studied and practical anion exchange, cation exchange and paper chromatographic procedures have been developed. Most of these have been applied to radioactive iron isotopes, especially in carrier-free separations for which these procedures are well suited.

Anion Exchange

Moore and Kraus(56) found that ferric iron is strongly adsorbed into anion exchangers from relatively concentrated hydrochloric acid solutions as the negatively charged chloro-complex. This property allows it to be easily separated from elements such as the alkali and alkaline earth metals which do not form such complexes. Aluminum, chromium and the rare earths are practically not adsorbed under these conditions and effective separations can be obtained. Marcus(57) studied the effect of various concentrations of iron (as low as 10^{-3} M), chloride and hydrogen (from 1-12 M) ions and obtained the stepwise formation contants. The exchange was independent of the iron concentration. Gruverman and Kruger(58) and Kraus and Moore(59) give procedures for separating iron and manganese using anion exchange. The ions are adsorbed onto Dowex 1 from concentrated hydrochloric acid solution, Mn is eluted with 4 N HCl and Fe is eluted with 0.5 N HCl. Anion exchange also has been used to separate Fe and Co(60) and to determine Ni, Mn, Co and Fe in high temperature alloys(61). Kakihana and Kajima(62) developed a procedure for separating iron and aluminum on an anion exchange column in which the iron is reduced to the ferrous state for elution. Studies of the adsorption of about 60 elements onto Dowex 1x10 resin from nitric acid solutions have been reported(63) and the optimum acid concentration for separation of Fe and Pu given as 8-12 N. Teicher and Gordon(64) separated iron and aluminum by retaining the iron on an anion exchanger as a thiocyanate complex while the aluminum was washed out. Procedure 3, Section VII of this report makes use of anion exchange.

Cation Exchange

Cation exchangers are used in iron separations in which some metal ions in solution are complexed and pass freely through the column while the uncomplexed ions are retained on the column. Selectivity is achieved by proper choice of complexing agent, and proper choice and control of the pH of the solution. Fritz and Umbreit(65) used ethylene diaminetetraacetic acid (EDTA) and found no exchange of iron in the pH range from 0.6 up to at least 4.0. Ryabchikov and Osipova(66) used various complexing agents to separate Mg, Al, Cr, Mn, Fe, Ni and Cu with rhodanide used to accomplish the final compexation of chromium and effect its separation from iron. From a perchlorate solution of iron, titanium, zirconium and hafnium, the latter three metals are adsorbed onto the anion exchange resin while iron passes freely through to effect a separation(67). Fritz and Karraker report(68) cation exchange group separations procedures using ethylenediammonium perchlorate solutions as eluants. Iron is separated with the divalent ions since ferric iron may be reduced on the column under this conditions. Good separation of iron from bismuth, thorium and zirconium is obtained.

Kraus, Michelson and Nelson(69) have observed a strong adsorption of the negatively charged ferric chloride complex by a cation exchange resin (Dowex 50) from concentrated chloride salt solutions. The distribution coefficient was greater than 10^4 for trace amounts. They separated ferric iron from 2 M $ZnCl_2$ solution containing excess hydrochloric acid, but the ferric iron concentration had to be less than 10^{-4} M or breakthrough occurred.

Paper Chromatography

Although paper chromatography has not been used extensively for radiochemical separations, it has been widely studied and applied to many conventional separations problems, some of the results of which would equally benefit radiochemical studies. Lederer and Lederer(70) and Block, Durrum and Zweig(71) have reviewed the application of paper chromatography to the study of inorganic ions. As in the case of ion exchange, selective separation is usually obtained by proper choice of complexing agent, pH and eluting agent, with a wider selection of eluting agents being generally available in paper chromatography. In some cases plain paper is used, in other cases the paper is pretreated with other adsorbing, ion exchange or complexing agents. Fe^{55} and Co^{60} can be separated by paper chromatography using an acetone-HCl-water (90:5:5) solvent with which the iron was eluted providing a carrier-free separation from the cobalt(72). Warren and Fink(73) have studied 17 cations with 10 developing solutions to obtain R_f values and enable conditions for paper chromatographic separation to be determined. Both chloride and tartrate complexes were used for complexing the iron. Ferrous and ferric iron were found to be separable by this technique. Other procedures have been reported for separating ferrous and ferric iron as acetates with n-butanol-ethanol-acetic acid and water (40:25:25:35) as solvent(74), as chloride complexes with ether-methanol-HCl-water as solvent(75), and as chloride complexes with butanol-12 N HCl (85:15) as solvent(76). Cu and Fe in the form of their benzoylacetone complexes can be completely separated on paper(77). The use of thenoyltrifluoroacetone complexes allows the separation of Fe(III), Co(II) and Ni(II); and Fe(III), Ni(II) and Mn(II) on plain paper using benzene-methanol (95:5) solvent, and the separation of Fe(III), Ni(II) and Mn(II) on alumina impregnated paper using methanol-benzene-acetic acid (10:88:2) solvent(78).

8. Electrochemical Behavior of Iron

Electroanalytical methods are widely used for the determination of iron. These methods are reviewed by Lingane(79). Some of these techniques are of interest in the radiochemistry of iron, particularly separations by electrodeposition into a mercury cathode and electroplating onto metal disks for counting purposes.

Iron was one of the first metals deposited on a mercury cathode(80) and this technique is probably the most common application of the mercury cathode. The deposition is quantitative for iron but is not very selective. A recent study by Bock and Hackstein(81) included electrodeposition of some 20 elements from a sulfuric acid solution and measured the interferences from these elements. A rapid separation of iron from Al, Ti, Zr, P, V and U is obtained by deposition of the iron in a mercury cathode from 1 N H_2SO_4 solution(82). Because of the difficulty in removing the iron quantitatively from the mercury and the difficulties associated with counting the radioisotopes of iron in a mercury medium, this technique is of greatest use for removing iron radioisotopes from solution prior to other analyses, but not so useful as an analytical method for the iron radioisotopes. Some practical applications of this to uranium solutions are given by Casto(83).

Electrodeposition of iron has been used for the preparation of radioiron sources for gravimetric analysis and for radioassay. Hahn(84) and Atchison and Beamer(85) plated iron onto brass from an alkaline solution of ascorbic acid, ammonium hydroxide and sodium citrate. Peterson(81) electroplated iron onto copper disks from an ammonium oxalate-hydrochloric acid solution of initial pH of 4 and final pH of 8. Peacock et al(86) and Maletskos and Irvine(87) electroplated from an ammonium oxalate-sulfuric acid solution of initial pH of 4 and final pH of 7. In the last study referenced,it was found that thiocyanate, phosphate and calcium ions must be absent for quantitative electroplating of iron.

V. DISSOLUTION OF SPECIAL IRON CONTAINING MATERIALS

In general, standard procedures for bringing iron containing samples into solution can also be used for radioanalytical sample preparation since they all result in iron's presence in the ferrous or ferric form,and no difficulty is encountered in getting the inert carrier iron and the radioactive iron in the same chemical form. The standard dissolution procedures are given in Snell and Snell(88), Sandell(31) and Hillebrand and Lundell(89). Dissolution methods for uranium and its compounds for iron determinations are given by Bane and

Grimes(90). It is usually desirable in radiochemical work to dissolve the sample completely rather than to rely on leaching of a residue. In some cases this requires a fusion. In fusions in platinum, particularly at high temperatures and under reducing conditions, iron can be lost to the platinum crucible. Not only does this loss affect the current sample, but since the iron later may be released in other fusions it affects subsequent analyses. This difficulty is avoided in those samples where wet digestion is not sufficient by heating no higher than 700°C and in an oxidizing atmosphere. Snell(91) suggested the use of a silver crucible and a flux consisting of equal amounts of sodium carbonate and sodium borate.

Many sample preparation methods have been used for iron determinations in organic and biological samples. These methods were reviewed by Gorsuch(92), and eight representative methods for trace elements in biological material were assessed using radioactive tracers for 14 elements, including iron. He found that wet oxidation of organic material with nitric and perchloric acids was the most satisfactory for all the elements studied, with the exception of mercury. No clear cut recommendation was made on dry oxidations, but use of a low-temperature of 500-550°C seemed to be most favorable, with some loss of iron reported at higher temperatures.

VI. COUNTING TECHNIQUES FOR IRON NUCLIDES

Fe^{52} and Fe^{53} emit positrons, and Fe^{59} and Fe^{61} emit negatrons with sufficient energy to allow accurate assay by the usual techniques of beta counting. The energy of the Fe^{60} beta radiation has not yet been determined. Fe^{52} and Fe^{53} decay into the radioactive manganese daughters, Mn^{52} (21.3 m) and Mn^{53} ($\sim 1.4 \times 10^2$ y). Mn^{52} decays by emitting 2.63 Mev positrons and two gamma rays of 1.45 and 0.39 Mev which must be considered in counting the Fe^{52}. Because of the short half-life of the Mn^{52} daughter, it is probably best to allow it to build into equilibrium (1-1/2 to 2 hours) before radioassay of the Fe^{52}. Because Mn^{53} decays by electron capture and has such a long half-life, it need not be considered in counting Fe^{53}. Fe^{60} decays to Co^{60m} and can be determined by chemically isolating the Co^{60m} and counting the positrons (0.28 percent of the transitions) or the 59 kev γ rays(93).

Fe^{52}, Fe^{53}, Fe^{59} and Fe^{61} can be radioassayed by gamma counting, but in the cases of Fe^{52} and Fe^{53} the uncertainties in the decay schemes would not allow absolute determinations. Since Fe^{52} and Fe^{53} decay by positron emission, they can be radioassayed by regular or coincidence gamma counting techniques on their annihilation radiations.

Fe^{55} and Fe^{59} are the iron nuclides measured in neutron activation studies and are the iron isotopes most used for tracer studies. Fe^{59} is perhaps most commonly used as an iron tracer because it can be readily assayed by beta or gamma counting. Fe^{59} and Co^{60} are often found together in solutions to be analyzed and present an unusual problem in gamma counting, since the 1.098 and 1.289 Mev gamma rays from Fe^{59} and the 1.173 and 1.333 Mev gamma rays from Co^{60} present interfering spectra on gamma scintillation counting. This problem can be resolved by coincidence techniques, since the Co^{60} gamma rays are emitted in cascade and can be coincidence counted while those from Fe^{59} are not in cascade(94).

Fe^{55} is a pure electron capture isotope emitting X-radiation with a maximum energy of 5.6 kev which is usually counted by thin window (or windowless) proportional counters or thin crystal scintillation counters(86,95,96). The ratio of Auger electrons to K X-rays is 3:1(97). If windowless counters are used, the Auger electrons are counted with good efficiency making the overall efficiency for Fe^{55} counting as high as 47 percent in a 4π proportional counter(98). The longer half-life and softer radiation of Fe^{55} give it a definite advantage over Fe^{59} in biological work, and in some cases advantages are obtained by using the two nuclides together in dual tracer experiments(86,99). For counting mixtures of Fe^{55} and Fe^{59}, Peacock et al(86) have devised a method of discriminating against either nuclide by employing G.M. tubes of different characteristics. Fe^{59} can be preferentially detected by means of a helium-filled tube with a thin mica window. An argon-filled tube with a beryllium window serves as a detector that is mainly sensitive to Fe^{55}. Rediske et al(99) use a proportional counter to obtain the total Fe^{55} plus Fe^{59} count, then they count through a 0.63 mg per sq cm rubber hydrochloride absorber which reduces the Fe^{55} count to 1.5 percent while only reducing the Fe^{59} count to 66 percent. From these data the amounts of both nuclides were determined. Stewart and Rossi(96) reduce the Fe^{59} count to 3 percent by means of a magnetic field, without effecting the Fe^{55} counting rate, as a means of determining the two nuclides in mixtures.

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR IRON

PROCEDURE 1

Source: F. L. Moore, W. D. Fairman, J. G. Ganchoff and John G. Surak, Anal. Chem. 31, 1148 (1959).

Sample Type: Homogeneous reactor solution.

Advantages: Excellent decontamination from a wide variety of radioisotopes. May be adapted to remote control operation.

Yields: 70-80 percent.

Procedure:

1. Place sample in 50 ml Lusteroid tube. Add 20 mg ferric iron carrier. Stir well and precipitate ferric hydroxide by adding excess concentrated ammonium hydroxide. Centrifuge for 1 minute in a clinical centrifuge and discard the supernatant solution.
2. Wash precipitate by stirring with 15 ml of 1 M ammonium hydroxide. Centrifuge for 1 minute and discard the supernatant solution.
3. Dissolve the ferric hydroxide in 3 ml of concentrated nitric acid. Add 10 ml of 10 M nitric acid and 1.3 ml of hydrogen peroxide (30 to 35 percent). Mix well.
4. Add 15 ml of 0.5 M 2-thenoyltrifluoroacetone-xylene, and extract for 5 minutes. Centrifuge for 1 minute and carefully remove the aqueous phase with a transfer pipet attached by rubber tubing to a vacuum trap.
5. Wash sides of the tube with several milliliters of distilled water from a wash bottle. Centrifuge for one minute and withdraw aqueous wash solution.

6. Transfer the organic phase to a clean tube and perform 1 minute scrubs with 15 ml portions of the following solutions. After each wash, centrifuge for 1 minute, withdraw the aqueous wash solution, and wash the sides of the tube with several milliliters of distilled water.
   a. Four M nitric acid - 3 percent hydrogen peroxide. Perform two scrubs and transfer the organic phase to a clean tube after the second scrub.
   b. 0.25 M hydrofluroic acid - 0.25 M nitric acid. Perform four scrubs and transfer the organic phase to a clean tube after second and fourth scrubs.
7. Add 5 ml of concentrated hydrochloric acid solution and mix thoroughly until the organic phase is essentially decolorized. Centrifuge for 1 minute and remove most of the organic phase with mild suction.
8. Wash sides of the tube with several milliliters of xylene from a wash bottle and centrifuge for 1 minute. Withdraw organic phase.
9. Precipitate ferric hydroxide by the addition of excess concentrated ammonium hydroxide. Filter, transfer precipitate to a porcelain crucible and ignite at 700°C for 30 minutes. Transfer to a tared aluminum foil and weigh.
10. Fold foil and place in tube for gamma spectrometric analysis.

PROCEDURE 2

Source: R. W. Perkins, accepted for publication in Talanta (1960).

Sample Type: Reactor coolant water containing activated process water chemicals, activated corrosion products, and fission products. Also applicable to aluminum metal samples.

Advantages: Procedure designed to take advantage of gamma spectrometry. High yield, short procedure.

Yield: About 90 percent.

Procedure:

1. Where necessary, dissolve sample in nitric acid or aqua regia. Add 3 ml of perchloric acid and evaporate to 1 ml.
2. Add 10 ml of concentrated nitric acid and heat to boiling.

3. Add 2 ml distilled water to bring the nitric acid concentration to 12 N and extract with an equal volume of 0.45 M 2-thenoyltrifluoroacetone in benzene by shaking for 15 minutes.
4. Separate and wash organic layer three times with equal volumes of 3 N nitric acid, shaking for 5 minutes each time.
5. Plate organic layer on a one inch counting dish for gamma spectrometric analysis.*

PROCEDURE 3

Source: A. L. Boni, Anal. Chem. 32, 599-604 (1960).

Sample Type: Water, vegetation, soil and biological materials containing fission product and neutron acitivated radionuclides. (Cr, Sr, RE, Cs, I, Ru, ZrNb, Np, Co, Fe, Zn)

Advantages: A sequential separation scheme based largely on anion exchange techniques to achieve decontamination factors of about 10^4.

Yield: 99 percent with a precision of ± 2.5 percent at the 90 percent confidence limit.

Procedure:

1. Obtain sample in a 25 ml solution of 3 N hydrochloric acid - 0.1 N hydrofluoric acid. Water samples are evaporated to dryness and residue dissolved directly or following acid digestion on a hot plate (insoluble residue filtered off and discarded). Soil samples are treated as water sample residue. Vegetation and biological samples are ashed in a muffle furnace, then dissolved or leached with HCl-HF solution.
2. To sample in a 50 ml Erlenmeyer flask add 10 mg chromium carrier, 25 mg ruthenium carrier and adjust volume to 35 ml with water. Add 1 ml of a 0.2 gram per ml thioacetamide solution and heat to 90-100°C until the precipitate settles to the bottom and the supernate clears. (About 45 minutes)

---

* Perkins, R. W., Gamma-Ray Spectrometric Systems of Analysis, Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva 1958, p/2377, Vol. 28 p 445, United Nations, Geneva (1958).

3. Filter through HA Millipore filter and wash with 2 N hydrochloric acid - 0.08 N hydrofluoric acid solution. Finally wash with ethanol. (The precipitate contains the ruthenium and iodine which can be determined by further treatment.)
4. Evaporate filtrate to dryness with concentrated nitric acid to drive off iodine. Take up sample in 20 ml concentrated hydrochloric acid and pass through a 0.9x13 cm column of Dowex 2x8, chloride form anion exchange resin and wash with 40 ml concentrated hydrochloric acid. (Effluents contain Cr, Sr, RE and Cs.)
5. Elute Zr-Nb, Ru and Co from the resin with the addition of 40 ml of 6.0 N hydrochloric aci - 0.5 N hydrofluoric acid solution.
6. Elute iron from the column with 30 ml 0.5 N hydrochloric acid. (Zinc remains on the column and may be eluted with 0.005 N hydrochloric acid.)
7. Evaporate iron effluent to 2 ml and place in vial for well-crystal scintillation counting.

PROCEDURE 4

Source: F. G. Lowman, R. F. Palumbo and D. J. South, U.S.A.E.C. Report No. UWFL-51. June 21, 1957.

Sample Type: Plant and animal tissues containing radioisotopes from bomb debris.

Advantages: Ion exchange separation techniques together with gamma spectrometry provide simple analytical methods for Fe^{55} and Fe^{59} and other components in a complex mixture of radioisotopes.

Yield: Quantitative

Procedure:

1. Dry and dry ashed samples weighing 0.1-2.5 g were wet ashed using different treatment depending on the sample type. Clam kidneys were digested in 0.2 N hydrochloric acid. Fish livers were digested in aqua regia or concentrated perchloric and nitric acid mixtures. Soil was ashed in concentrated hydrochloric acid. The samples were than evaporated to

dryness and redissolved in 0.1-0.2 N hydrochloric acid. The sample was filtered and an aliquot used for radioassay.

2. Pass solution through a 6x100 mm ion exchange column (Dowex-50, prewashed with 3 column volumes of 0.1 N hydrochloric acid) at a rate of 0.2-0.5 ml per minute. Wash column with 20-60 ml hydrochloric acid of same normality as sample solution. (This wash removed Ru^{106}-Rh^{106} and Zr^{95}-Nb^{95}.)
3. Elute iron fraction (also remaining Zr^{95}-Nb^{95}) with 0.5 percent oxalic acid solution. Determine Fe^{55} in methane gas flow counter and Fe^{59} by gamma spectrometry.
4. Citric acid solutions of different pH are subsequently used to elute the remaining isotopes, Cs^{137}, Ce^{144}-Pr^{144}, rare earths, Zn^{65}, Co^{60}, Mn^{54} and Sr^{90}.

PROCEDURE 5

Source: W. H. Hutchin, U.S.A.E.C. Report No. UCRL-4377, pp 20-21, August 10, 1954.

Sample Type: Nine-day old solution of $4x10^{13}$ fissions with 10^7 atoms Fe^{59}.

Advantages: Isolated Fe^{59} showed no evidence of contamination by other radionuclides after three half lives.

Yield: About 70 percent.

Procedure:

1. To the active solution add 10 mg Fe carrier and 1 to 2 ml saturated tartaric acid solution. Make basic with NH_4OH. Saturate with H_2S and centrifuge and discard supernatant. Wash precipitate twice with a solution of dilute NH_4OH saturated with NH_4NO_3.
2. Dissolve FeS in about 1/2 milliliter concentrated HCl. Boil to drive off H_2S. Add one drop HNO_3. Boil to get rid of nitrate ion, adding more HCl if necessary. Reduce volume to 0.5 ml. Bring volume to 4 ml with concentrated HCl.

PROCEDURE 5 (CONTINUED)

3. Put on an anion column (Dowex 1x8, 50-100 mesh) that has been washed with concentrated HCl. Wash with 4 ml of 12 M HCl, 4 ml 6 M HCl. Elute with 4 ml of 5 M HCl. (Anion column is 3 inches long by 1/4 inch i.d.)
4. To the eluate add 5 mg Cu^{++} carrier, a drop of Sb^{+3}, As^{+3}, Te^{+4} carriers. Add 0.5 M HCl to bring volume to 20 ml. Saturate with H_2S. Centrifuge and discard precipitate.
5. Add 1-2 ml saturated tartaric acid solution, make basic with NH_4OH and saturate with H_2S. Centrifuge and discard supernatant. Wash precipitate twice with NH_4OH-NH_4NO_3 solution to prevent peptization.
6. Dissolve precipitate in concentrated HCl. Add a drop of concentrated HNO_3 to complete solution. Boil to destroy HNO_3 and reduce volume to $\sim$1 ml. Add 6 N HCl to bring volume to $\sim$15 ml and add Hg metal (0.5 ml). Stir for $\sim$5 minutes to reduce Fe^{+3} to Fe^{+2}. Extract twice with equal volumes of diisopropyl ether. Discard ether layers.
7. Pipet aqueous layer away from Hg and centrifuge off the remaining Hg. Add 1 ml of saturated tartaric acid solution and make basic with NH_4OH. Pass in H_2S, centrifuge and discard supernatant. Wash precipitate twice with NH_4OH-NH_4NO_3 solution.
8. Dissolve in about 1 ml concentrated HCl. Add two or three drops of concentrated HNO_3 and boil to small volume. Add more concentrated HCl and boil to small volume again (0.5 ml). Bring volume to 15 ml with 8 M HCl and extract twice with equal volumes of diisopropyl ether. Combine ether layers and wash once with 8 M HCl.
9. Equilibrate the combined ether layer with two 10 ml portions of water. Separate and discard ether layer.
10. Make the solution ammoniacal, centrifuge and discard supernatant. Wash precipitate twice with acetone, stir moist precipitate while in hot water bath until dry and finely divided. Ignite for 10 minutes in a porcelain crucible over a Fisher burner. Cool and weigh as Fe_2O_3.

PROCEDURE 6

Source: J. S. Gilmore, U.S.A.E.C. Report No. LA-1721, Sept. 10, 1954.

Sample Type: Iron radioisotopes in fission product solutions.

Advantages: Combination of precipitations, extractions and electroplating achieves high order of decontamination necessary for beta counting of Fe^{59}.

Yield: About 50 percent.

Procedure:

1. To the sample in a 40 ml conical centrifuge tube, add 4.0 ml of standard Fe carrier. Make the solution ammoniacal with concentrated NH_4OH and add 5 ml of $(NH_4)_2S$ solution. Centrifuge and discard the supernate.
2. Dissolve the FeS precipitate in 3 to 4 drops of concentrated HCl and boil the solution to drive off H_2S. Add 10 mg each of Te(IV), Sn(II) and Sb(III) carriers, and 20 ml of 0.2 M HCl. Add 1 drop of 0.1 percent of Aerosol solution and saturate with H_2S. Filter into a clean 40 ml centrifuge tube and discard the precipitate.
3. To the filtrate add 1 to 2 ml of saturated tartaric acid and 5 ml of $(NH_4)_2S$ solution. Centrifuge and discard the supernate.
4. Dissolve the precipitate in 3 to 4 drops of concentrated HCl and oxidize the ferrous ions with 1 to 2 drops of concentrated HNO_3. Evaporate the solution to dryness; add 3 to 4 drops of concentrated HCl, and again evaporate to dryness. Transfer the $FeCl_3$ with the aid of 10 ml of 8 M HCl to a 125 ml separatory funnel. Add 30 ml of isopropyl ether, shake for 1 minute, and discard the aqueous phase. Add 10 ml of H_2O to the ether phase and shake for 1 minute. Transfer the aqueous phase to a 40-ml centrifuge tube and discard the ether layer.
5. To the aqueous phase add 1 ml of saturated tartaric acid and 5 ml of $(NH_4)_2S$ solution. Centrifuge and discard the supernate.
6. To the FeS precipitate add 3 to 4 drops of concentrated HCl and boil to remove H_2S. Add 10 mg of Sb(III) carrier and 3 to 4 drops of liquid Br_2. Boil off excess Br_2, and add 10 mg of Tl(III) carrier and 10 mg of carrier (NOTE 1). Make the solution up to a volume of 20 ml with 0.2 M HCl, add

1 drop of aerosol solution, and saturate with H_2S. Filter into a 40 ml centrifuge tube and discard the precipitate.

7. Repeat steps 3, 4 and 5.
8. Dissolve the FeS precipitate in 1 ml of concentrated HCl. Boil, add 1 ml of Te(IV) carrier and boil again (NOTE 2). Dilute the solution to 20 ml with 0.2 <u>M</u> HCl. Add 10 mg each of Sn(II) and Sb(III) carriers, 1 drop of aerosol solution, and saturate with H_2S. Filter into a 40 ml centrifuge tube and discard the precipitate.
9. Repeat steps 3, 4, 5 and 6.
10. Repeat steps 3 and 4.
11. Filter the aqueous layer into a clean 40 ml centrifuge tube and precipitate $Fe(OH)_3$ with concentrated NH_4OH. Centrifuge and discard the supernate.
12. To the precipitate add 1 ml of $NH_4H_2PO_4$ reagent, 10 ml of $(NH_4)_2CO_3$ reagent, and warm to dissolve the $Fe(OH)_3$. Transfer the solution to a plating cell.
13. Plate on a 1 inch Pt disk for 1 hour at 2 amp and 70°C. Wash the plate with H_2O and with 95 percent ethanol. Dry in over at 100°C for 5 minutes, cool, weigh and beta-count.

Notes

1. To promote exchange between radioantimony and carrier, Sb(III) is first oxidized to Sb(V) by Br_2 and the pentapositive antimony is then reduced by iodide ion. In the nest operation H_2S reduces Tl(III) to Tl(I) which is then precipitated as the iodide.
2. When the solution containing Te carrier is boiled with concentrated HCl, any Te(VI) present is reduced to the +4 state. This operation promotes exchange.

PROCEDURE 7

Source: W. A. Brooksbank, Jr., U.S.A.E.C. Report No. ORNL-2226, pp 23-35, Dec. 1956.

Sample Type: Iron impurity in aluminum metal. Fe^{59} isolated and measured following neutron bombardment.

Advantages: Fe^{59} determined in presence of neutron activation isotopes of Cu, Mn, Ni, Zn, Ti, Co, Ag, Zr and Sb.

Yield: 80 percent.

Procedure:

1. Allow activated sample to stand for one week to allow decay of 15-hour Na^{24}.
2. Treat 2-3 g aluminum samples (containing milligram quantites of iron) in 50 ml centrifuge tubes with 3 ml of 19 M sodium hydroxide. After 5 minutes add 3 ml of distilled water. When dissolution has ceased, heat tubes to boiling and hold for 3 minutes. After solution has cooled to room temperature, acidify with 12 M hydrochloric acid to obtain clear solution.
3. Add one milliliter (10 mg) iron carrier, and holdback carriers of yttrium, copper(II), zinc, cobalt, strontium and manganese(II).
4. Precipitate copper sulfide by passing in H_2S and filter. Remove excess sulfide from the filtrate by boiling with concentrated nitric acid and bromine water.
5. Precipitate ferric hydroxide by adding 15 M aqueous ammonia, filter and wash precipitate with ammonia.
6. Dissolve precipitate in 1 M hydrochloric acid and reprecipitate with 8 M sodium hydroxide. Wash precipitate free of sodium hydroxide.
7. Dissolve precipitate in 8 M hydrochloric acid and extract the acid solution once with an equal volume of isopropyl ether.
8. Strip iron from the organic phase with water and repeat steps 5 and 6.
9. Ignite precipitate for twenty minutes at 700°C.
10. Dissolve sample with 3 M nitric acid and add dilute hydrofluoric acid to precipitate yttrium fluoride. Centrifuge and discard rare earth fluoride.
11. Reprecipitate ferric oxide, transfer to tubes for discriminatory gamma counting.

PROCEDURE 8

Source: J. R. Klein and P. Bianchi, Archives of Biochemistry and Biophysics 55, 157-161 (1955).

Sample Type: Animal tissues.

Advantages: Radioiron is quantitatively isolated from animal tissues for beta or X-ray counting without requiring an electroplating step.

Yield: About 99 percent.

Procedure:

1. Digest tissue samples with sulfuric acid and hydrogen peroxide and then dilute to give a final acid concentration of 6.5 N and total iron content in a range suitable for colorimetric iron assay using dipyridyl. Determine total iron concentration.
2. Add carrier iron to diluted digest to make a total of 20 μM iron, adjust volume to 50 ml with cold 6.5 N sulfuric acid and place in 125 ml separatory funnel, the stopcock of which is lubricated with water.
3. Cool solution to below 10°C and maintain at this temperature while performing four successive cupferron-chloroform extractions, adding 0.06 g cupferron in water solution for each extraction and extracting with 5.5, 3 and 2 ml of chloroform, collecting extracts in a 30 ml Kjeldahl flask.
4. Add 10 ml water, boil off chloroform, add 8 drops concentrated sulfuric acid and 10 drop concentrated nitric acid and wet ash with further addition of 10 drops of nitric acid and several additions of 1 drop each of 30 percent hydrogen peroxide. Boil digest with 5 ml water to dissolve any solid.
5. Transfer solution to a 12 ml conical centrifuge tube, add 10 drops concentrated NH_4OH to precipitate ferric hydroxide and centrifuge. Without breaking up the precipitate, wash tube with 5 ml water, drain, heat to 80-90°C to remove the major portion of the water in the precipitate.
6. Add 1 ml 0.16 N sulfuric acid and heat briefly at 50°C to effect solution without excessive evaporation.
7. Plate a 0.5 ml aliquot in a glass or stainless steel sample holder coated with silicone stopcock grease, add 1 drop of 1 percent Duponol solution,

and then precipitate the iron by adding 1 drop of concentrated NH_4OH solution. Evaporate to dryness and beta or X-ray count for Fe^{59} or Fe^{55}.

PROCEDURE 9

Source: A. W. Kenny, W. R. E. Maton and W. T. Spragg, Nature <u>165</u>, 183 (1950).

Sample Type: Fe^{59} formed in cobalt by n,p reaction.

Advantages: Fe^{59} obtained carrier-free and with no other radioisotopes.

Yield: Quantitative.

Procedure:

1. Dissolve cobalt metal sponge in 3 <u>N</u> nitric acid. Add ammonia and ammonium acetate to adjust pH to range of 4.0-7.0.
2. Add 1 drop acetylacetone and extract with xylene. Separate organic phase.
3. Wash organic phase with water and evaporate to dryness. Destroy any charred residue by fuming with perchloric acid.
4. Take up residue in dilute hydrochloric acid.

PROCEDURE 10

Source: J. D. Gile, W. M. Garrison, J. G. Hamilton, U.S.A.E.C. Report No. UCRL-1315, May 18, 1951.

Sample Type: 10 mil thick cobalt foil containing less than 20 ppm iron bombarded by 20 Mev deuterons to form Fe^{59} by the d,2p reaction on Co^{59}.

Advantages: Fe^{59} obtained carrier-free and free from other radioisotopes.

Yield: 98 percent.

Procedure:

1. Dissolve cobalt (about 100 mg) in 12 <u>N</u> hydrochloric acid, centrifuge and discard residue.
2. Dilute solution with an equal volume of water and adjust to a pH of 9 with 15 <u>N</u> NH_4OH to give a clear "solution".

3. Pass solution through Whatman No. 50 filter paper to absorb colloidal iron.
4. Wash filter with dilute NH_4OH until cobalt is not detected in the filtrate, then wash with distilled water.
5. Remove Fe^{59} with 6 N hydrochloric acid.

PROCEDURE 11

Source: J.C. Roy and T. P. Kohman, Can. J. Physics 35, 649 (1957).

Sample Type: Copper bombarded with 400 Mev protons for 200 hours at about 1 μ amp and allowed to decay 5 months.

Advantages: Iron radioisotopes isolated including Fe^{60} which was determined by measuring Co^{60m} daughter.

Yield: About 80 percent.

Procedure:

1. Dissolve copper in concentrated nitric acid and evaporate to dryness. Add concentrated hydrochloric acid and evaporate to dryness twice.
2. Dissolve in 8 N hydrochloric acid, add carriers for Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Zn. Extract ferric chloride with isopropyl ether, wash ether phase with 8 N hydrochloric acid containing carriers for the elements above until the ferric solution is free from any radioactivities but iron. (Solution now has a millicurie of Fe^{59}, some Fe^{55} and Fe^{60}.) In order to determine the Fe^{60} an active daughter extraction was used and the Co^{60m} conversion electrons were counted in a thin window (or windowless) low background counter.
3. Extract ether solution of ferric chloride with two 5 ml portions of 8 N hydrochloric acid, the first containing 0.5 mg cobalt carrier.
4. Extract the aqueous solution three times with isopropyl ether to remove Fe^{59}.
5. Neutralize aqueous phase with ammonium hydroxide and pass in H_2S to precipitate CoS. Filter through Millipore filter allowing only air which has been previously Millipore filtered to pass through so as to not get

any short-lived radioisotopes from the air. Plate and count 51 kev conversion electrons.

PROCEDURE 12

Source: A. N. Murin, V. D. Nefedov, I. A. Yutlandov, Uspeckhi Khimii 24, 527-574 (1955) (AERE Lib/Trans 722)

Sample Type: Manganese dioxide containing less than 10^{-5} part iron bombarded with 10 Mev deuterons for 10 hours at 180 µA to produce Fe^{55} by the d,2n reaction on Mn^{55}.

Advantages: Fe^{55} obtained carrier-free and free from other iron radioisotopes.

Procedure:

1. After 3 weeks decay period dissolve target in warm 8 N hydrochloric acid.
2. Add a few milligrams of cobalt hold-back carrier and extract iron twice with isopropyl ether.
3. Wash ether fraction twice with 8 N hydrochloric acid and extract iron repeatedly with water.

PROCEDURE 13

Source: J. H. Rediske, R. F. Palmer and J. F. Cline, Anal. Chem. 27, 849-50 (1955).

Sample Type: Plant material.

Advantages: Simple procedure suitable for dual tracer (Fe^{55} and Fe^{59}) analysis. Analysis carried out on same solutions used for the thiocyanate colorimetric analysis of total iron (Sandell, E. B., "Colorimetric Determination of Traces of Metals", Interscience, New York, 1950).

Procedure:

1. Wet ash 1-2 g sample of plant material in a Kjeldahl flask with concentrated sulfuric acid and enough perchloric acid to clear (Piper, C. S., "Soil and Plant Analysis", Interscience, New York, 1944).
2. Boil off excess water, allow flasks to cool, and dilute digest with water to an approximate concentration of 20 percent sulfuric acid and a known total volume.

3. Transfer a 1 ml aliquot to a 15 ml test tube, add 10 mg ferric iron carrier and dilute with water. Add 1 ml of 20 percent potassium thiocyanate in water, then layer on the aqueous phase 2 ml of a solution of equal parts by volume of diethyl ether and isoamyl alcohol.
4. Shake tube 5 to 10 times and allow phases to separate for 3-5 minutes. Remove a 0.1 to 1 ml aliquot of the organic phase and pipet onto a stainless steel dish. Dry under an infrared lamp, flame lightly over a Bunsen burner and count on windowless flow proportional counter with and without a 0.63 mg per sq cm rubber hydrochloride absorber to determin the Fe^{55} and Fe^{59}.

REFERENCES

1. J. O. Julians, C. W. Kocher, T. D. Nainan, and A.C.G. Mitchell, Phys. Rev. 113, 602-8 (1959).

2. E. Ricci, J. P. Campá, and N. Nussia, Publs. com. nacl. energiá atomica (Buenos Aires) Ser. quim. 1, 129-40 (1947).

3. J. D. Gile, W. M. Garrison and J. G. Hamilton, UCRL-1315, University of California Radiation Laboratory, Berkeley, California, May 18, 1951.

4. H. N. Stokes and J. R. Cain, J. Am. Chem. Soc. 29, 409 (1907).

5. H. H. Willard, Anal. Chem. 22, 1372 (1950).

6. H. H. Willard and J. L. Sheldon, Anal. Chem. 22, 1162 (1950).

7. L. Ginsburg, K. Millar and L. Gordon, Anal. Chem. 29, 46-8 (1957).

8. R. E. Peterson, Anal. Chem. 24, 1850 (1952).

9. S. C. Schome, Analyst 75, 27 (1950).

10. H. M. Irving and R. J. P. Williams, Analyst 77, 813 (1952).

11. H. M. Irving and R. J. P. Williams, J. Am. Chem. Soc. 2192 (1953).

12. M. Calvin and N. C. Melchior, J. Am. Chem. Soc. 70, 3270 (1948).

13. D. P. Mellor and L. Maley, Nature 159, 370 (1947).

14. D. P. Mellor and L. Maley, Nature 161, 436 (1948).

15. "Stability Constants of Metal-Ion Complexes, with Solubility Products of Inorganic Substances. Part I: Organic Ligands". Compiled by J. Bjerrum, G. Schwarzenback and L. G. Sillen, Special Publication No. 6, The Chemical Society, London (1957).

16. "Stability Constants of Metal-Ion Complexes, with Solubility Products of Inorganic Substances. Part II: Organic Ligands". Compiled by J. Bjerrum, G. Schwarzenback and L. G. Sillen, Special Publication No. 7, The Chemical Society, London (1958).

17. H. E. Wirth, Ind. Eng. Chem., Anal. Ed. 14, 724 (1942).

18. J. Mellan "Organic Reagents in Inorganic Analysis", pp 401-423, The Blakiston Company, Philadelphia, Pa. (1941).

19. W. B. Fortune and M. G. Mellon, Ind. Eng. Chem., Anal. Ed. 10, 60 (1938).

20. "The Iron Reagents: Bathophenanthroline, 2,4,6-Tripyridyl-s-triazine, and Phenyl-2-pyridyl Ketoxime", H. Diehl and G. F. Smith, the G. Frederick Smith Chemical Co., Columbus, Ohio (1960).

21. R. Abegg, Eisen, B. 385 (1935).

22. H. Cowling and E. J. Benne, J. Assoc. Offical Agr. Chem. 25, 555 (1942).

23. J. W. Rothe, Stahl u. Eisen 12, 1052 (1892).

24. G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry" p 118, John Wiley and Sons, Inc., New York (1957).

25. R. W. Dodson, G. J. Forney and E. H. Swift, J. Am. Chem. Soc. 58, 2573 (1936).

26. R. J. Myers, D. E. Metzler and E. H. Swift, J. Am. Chem. Soc. 72, 3767 (1950).

27. R. J. Myers and D. E. Metzler, J. Am. Chem. Soc. 72, 3772 (1950).

28. I. Wada and R. Ishii, Bull. Inst. Phys. Chem. Res. Tokyo 13, 264 (1934).

29. N. H. Nachtreib and J. G. Conway, J. Am. Chem. Soc. 70, 3547, 3552 (1948).

30. V. R. Bock and E. Bock, Z. anorg. Chem. 263, 146 (1950).

31. E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Rev., Interscience Publishers, Inc., New York (1959).

32. H. Specker and W. Doll, Z. anal. Chem. 152, 178 (1956).

33. V. W. Fischer and R. Bock, Z. anorg. Chem. 249, 146-197 (1942).

34. J. F. Steinbach, "Acetylacetone as an Analytical Extraction Agent", U.S.A.E.C. Report No. NYO-6347, University of Pittsburgh, Pittsburgh, Pa. (1953).

35. J. P. McKaveney, "Use of Acetylacetone Extractions in Ferrous Analysis", U.S.A.E.C. Report No. NYO-6507, Pittsburgh University, Pittsburgh, Pa. (1957).

36. A. W. Kenny, W. R. E. Maton and W. T. Spragg, Nature 165, 483 (1950).

37. E. Abrahamczik, Mikrochem. Mikrochim. Acta 33, 209 (1947).

38. J. P. McKaveney and H. Freiser, Anal. Chem. 29, 290 (1957).

39. J. C. Reid and M. Calvin, J. Am. Chem. Soc. 72, 2948 (1950).

40. R. A. Bolomy and L. Wish, J. Am. Chem. Soc. 72, 4483 (1950).

41. H. M. Irving, Quart. Rev. 5, 200-226 (1951).

42. M. Cefola and B. Miccioli, U.S.A.E.C. Report No. NYO-921, June 1, 1951.

43. E. Sheperd and W. W. Meinke, U.S.A.E.C. Report No. AECU-3879 (1958).

44. F. L. Moore, Am. Soc. Testing Materials Spec. Tech. Publ. No. 238, 13 (1958).

45. N. H. Furman, W. B. Mason and J. S. Pekola, Anal. Chem. 21, 1325 (1949).

46. E. B. Sandell and P. F. Cummings, Anal. Chem. 21, 1356 (1949).

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

48. R. Paulais, Compt. rend. 206, 783 (1938).

49. O. Baudisch and R. Furst, Ber. 50, 324 (1917).

50. J. Cholak, D. M. Hubbard and R. V. Story, Ind. Eng. Chem., Anal. Ed. 15, 57 (1943).

51. M. D. Foster, F. S. Grimaldi and R. E. Stevens, U.S. Geol. Survey, Rept. 2 (1944).

52. M. Zeigler, Naturwissenschaften 46, 492 (1959).

53. F. Kröhnke, Ber. 60, 527 (1927).

54. C. A. Kraus, U.S.A.E.C. Report No. A-1099, September 1944.

55. W. Korpak and C. Deptuka, U.S.A.E.C. Report No. NP-7238, Report No. 53/IV Polish Academy of Sciences, Institute of Nuclear Research, Warsaw, Dec. 1958.

56. G. E. Moore and K. A. Kraus, J. Am. Chem. Soc. 72, 5792 (1950).

57. Y. Marcus, J. Inorg. and Nucl. Chem. 12, 287 (1960).

58. I. J. Gruverman and P. Kruger, Inter. J. Appl. Rad. and Isotopes 5, 21 (1959).

59. K. A. Kraus and G. E. Moore, J. Am. Chem. Soc. 75, 1460 (1953).

60. H. L. Helwig, J. K. Ashikawa, H. Clokie and E. R. Smith, U.S.A.E.C. Report No. UCRL-2296, Radiation Laboratory, University of California, Berkeley, California, August 5, 1953.

61. J. L. Hague, E. E. Maczkowske and H. A. Bright, J. Research Nat'l. Bur. Standards 53, 353-9 (1954).

62. H. Kakihana and S. Kojima, Japan Analyst 2, 421 (1953).

63. R. F. Buchanan, J. P. Faris, K. A. Orlandini and J. P. Hughes, U.S.A.E.C. Report No. TID-7560, p 179-187 (1958).

64. H. Teicher and L. Gordon, Anal. Chem. 23, 930 (1951).

65. J. S. Fritz and G. R. Umbreit, Anal. Chim. Acta 19, 509 (1958).

66. D. I. Ryabchikov and V. F. Osipova, Zhur. Anal. Khim. 11, 278 (1956).

67. B. E. Marques and M. R. Grade, Las Ciencias, de Madrid 21, No. 3, 9 (1957).

68. J. S. Fritz and S. K. Karraker, Anal. Chem. 32, 957 (1960).

69. K. A. Kraus, D. C. Michelson and F. Nelson, J. Am. Chem. Soc. 81, 3204 (1959).

70. "Chromatography", E. Lederer and M. Lederer, 2nd Ed., Elsevier Publishing Company, New York (1957).

71. R. Block, E. Durrum and G. Zweig, 2nd Ed., Academic Press Inc., New York (1958).

72. M. Lederer, Anal. Chim. Acta 8, 134 (1953).

73. G. W. Warren and R. W. Fink, J. Inorg. Nucl. Chem. 2, 176 (1956).

74. H. M. Stevens, Anal. Chim. Acta 15, 538 (1956).

75. F. H. Pollard, Brit. Med. Bull. 10, 187 (1954).

76. C. Bighi, Ann. Chim. (Rome) 45, 532 (1955).

77. F. H. Pollard, J. F. W. McOmie, H. M. Stevens and J. G. Maddock, J. Chem. Soc. 1338 (1953).

78. E. W. Berg and R. T. McIntyre, Anal. Chem. 26, 813 (1954).

79. "Electroanalytical Chemistry", J. J. Lingane, 2nd Ed., Interscience Publishers, Inc., New York (1958).

80. O. W. Gibbs, Am. Chem. J. 13, 571 (1891).

81. R. Bock and K. G. Hackstein, Z. anal. Chem. 138, 339 (1953).

82. G. E. F. Lundell and J. I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, p 105 (1938).

83. C. J. Rodden, Editor-in-chief, "Analytical Chemistry of the Manhattan Project", McGraw-Hill Book Company, Inc., New York (1950).

84. P. F. Hahn, Ind. and Eng. Chem., Anal. Ed. 17, 45 (1945).

85. G. J. Atchison and W. H. Beamer, Anal. Chem. 24, 1812 (1952).

86. W. C. Peacock, R. D. Evans, J. W. Irving, Jr., W. M. Good, A. F. Kip, S. Weiss and J. C. Gibson, II, J.Clin.Invest. 25, 605 (1946).

87. C. J. Maletskos and J. W. Irvine, Jr., Nucleonics 14, No. 4, 84 (1956).

88. F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis", 3rd Ed. Vol. II, D. Van Nostrand Company, Inc., New York (1949).

89. W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis", John Wiley and Sons, Inc., New York (1950).

90. R. W. Bane and W. R. Grimes in "Analytical Chemistry of the Manhattan Project", C. J. Rodden, Editor-in-chief, McGraw-Hill Book Company, Inc., p 415 (1950).

91. H. R. Snell, Anal. Chem. 22, 326 (1950).

92. T. T. Gorsuch, Analyst 84, 135 (1959).

93. J. C. Roy and T. P. Kohman, Can. J. Phys. 35, 649 (1957).

94. E. Odeblad, L. Meurman and D. Ziliotto, Acta Radiol. 44, 337 (1955).

95. W. S. Lyon and S. A. Reynolds, Inter. J. Appl. Rad. and Isotopes 2, 80 (1957).

96. W. B. Stewart and H. H. Rossi, Nucleonics 11, No. 10, 66 (1953).

97. E. H. S. Burhop, "The Auger Effect", Cambridge University Press (1952).

98. R. A. Allen, Inter. J. Appl. Radiation and Isotopes 1, 289 (1957).

99. J. H. Rediske, R. F. Palmer and J. F. Cline, Anal. Chem. 27, 849 (1955).

USAEC Office of Technical Information Extension, Oak Ridge, Tennessee