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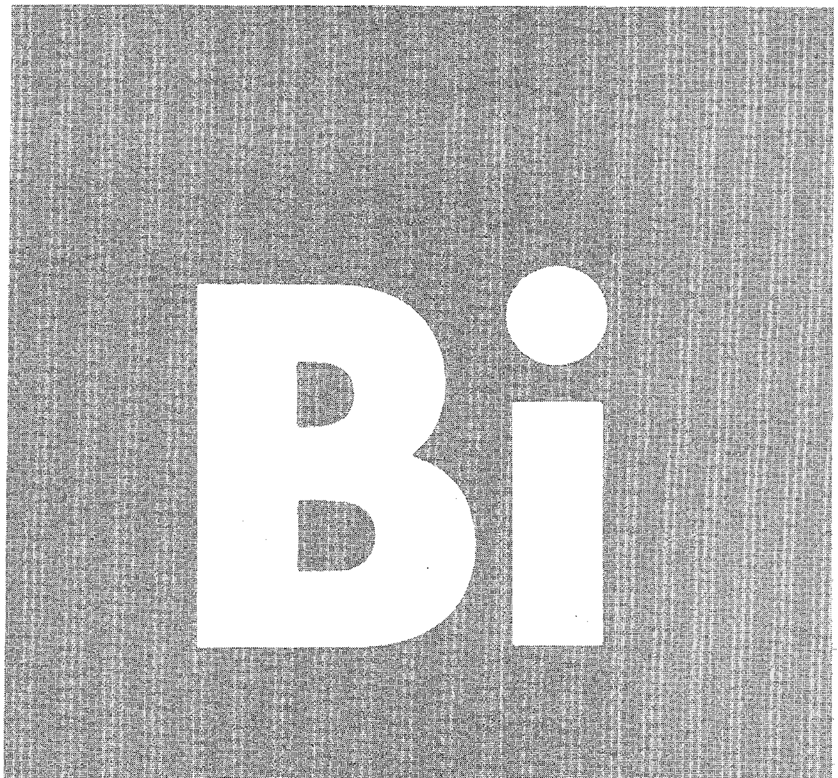

RADIOCHEMISTRY OF BISMUTH

NUCLEAR SCIENCE SERIES

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Radiochemistry of Bismuth

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Foreword

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science of the 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 radiochemical purity of reagents, radiochemistry in environmental science and in nuclear medicine, and the role of radiochemistry in college and university programs.

This series of monographs has grown out of the need for compilations of radiochemical information, procedures, and techniques. The Subcommittee has endeavored to present a series that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique.

Experts in the particular radiochemical technique have written the monographs. The Energy Research and Development Administration has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to radiochemists but also to research workers in other fields such as physics, biochemistry, or medicine who wish to use radiochemical techniques to solve specific problems.

G. Davis O'Kelley, *Chairman*
Subcommittee on Radiochemistry

Preface

This report on the radiochemistry of bismuth has been prepared as one of a series of monographs on the radiochemistry of the elements under the sponsorship of the Subcommittee on Radiochemistry of the Committee on Nuclear Sciences within the National Research Council.

Included herein is a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of important analytical procedures such as precipitation, solvent extraction, ion exchange, paper chromatography, electroanalytical separations, volatilization, etc., together with gravimetric, volumetric, and photometric methods and a discussion on problems of dissolution of a sample. Also included are various radioactivity counting techniques and a collection of radiochemical procedures for bismuth as found in the literature.

The information contained in this report is intended primarily for a radiochemist, but the increasing interest of the so-called radiochemist in problems involving mineral, meteorological, biological and environmental samples and the continuing use of radiochemical techniques by biologists, biochemists, analytical, organic and physical chemists has caused a rather broad definition of radiochemistry to be taken. It is hoped that this report will be of use to workers in these diverse fields, while at the same time keeping reasonably accessible the data needed by workers desiring to make simple, fast separations of bismuth from some other radioelements.

The literature search was completed around the middle of 1973.

It is hoped that the bibliography is sufficiently extensive to serve the needs of the radiochemist, but it is to be expected that important references were omitted. Notification of such omissions of published or unpublished material or new techniques for inclusion in future revisions of this monograph would be much appreciated by the author.

K. S. Bhatki

Bombay, India
March, 1976

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I. GENERAL REFERENCES ON THE CHEMISTRY OF BISMUTH

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II. ISOTOPES OF BISMUTH

TABLE I.

TABLE OF ISOTOPES OF BISMUTH

Isotope	Half-life or % Abundance	Type of Decay	Particle Energy (MeV)	Some Modes of Formation
$^{198}_{83}Bi$	1.7m	α	6.2	Deuterons on lead
^{197} or ^{198}Bi	7.8m	α	5.83	Protons on lead
^{199}Bi	24.4m	α (0.01%) EC (99%)	5.47 Lead X-rays	Protons on lead Parent ^{199m}Pb
^{200}Bi	35m	EC		Protons on Pb Parent ^{200}Pb; daughter ^{200}Po
^{201}Bi	1.85h	EC	Lead X-rays	Protons on Pb parent ^{201m}Pb;
^{201m}Bi	52m	α EC γ with ^{201m}Pb	5.28 0.6290	daughter ^{201}Po Parent ^{201}Pb
^{202}Bi	95m	EC γ	Lead X-rays 0.4220; 0.9610	daughter ^{202}Po

TABLE I. (Continued)

Isotope	Half-life or % Abundance	Type of Decay	Particle Energy (MeV)	Some Modes of Formation
^{203}Bi	11.8h	α	4.85	^{206}Pb(p,4n)^{203}Bi
		β^{+}	0.74; 1.35 max^{m}	parent^{203}Pb; and ^{203m}Pb.
		EC		
		γ(∼24 gammas)	0.186 (6%)	daughter^{203}Po
			0.264 (6%) 0.3814 (9%) 0.8197 (78%) 1.034 (16%) 1.52 (31%) 1.896 (35%) (doublet)	daughter^{207}At
^{204}Bi	11.2h	EC	Q_{EC} 4.4 est	^{206}Pb(p,3n)^{204}Bi
	11.6h	noβ^{+}; noβ^{-}	Lead X-rays	^{203}Tl(α,3n)^{204}Bi
		γ	0.21; 0.375	^{204}Pb(d,2n)^{204}Bi
			0.671; 0.9117;	parent^{204m}Pb
			0.9840; 1.211	daughter^{204}Po
^{205}Bi	15.3d	EC		^{206}Pb(d,3n)^{205}Bi
		β^{+}	0.98 max^{m}	^{209}Bi(p,5n)^{205}Po
			Lead X-rays	^{205}Po $\xrightarrow{EC}$ ^{205}Bi
		γ(∼38 gammas)	0.2605; 0.2842;	daughter^{205}Po
			0.3494; 0.3832;	and ^{209}At.
			0.5710 (14%); 0.7030 (28%); 0.9880 (17%); 1.766 (27%); 1.777	Parent^{205}Pb

TABLE I. (Continued)

Isotope	Half-life or % Abundance	Type of Decay	Particle Energy (MeV)	Some Modes of Formation
^{206}Bi	6.24d	EC		^{206}Pb(d,2n)^{206}Bi
		β^+		^{207}Pb(d,3n)^{206}Bi
		γ(∿31 gammas)	0.1841; 0.3430; 0.497 (18%); 0.516 (46%); 0.538 (34%); 0.803 (99%); 0.881 (72%); 0.895 (19%); 1.099; 1.596; 1.72 (36%)	^{205}Tl(α,3n)^{206}Bi ^{209}Bi(p,pxn)^{206}Bi daughter^{206}Po daughter^{210}At
^{207}Bi	∿30y	γ	0.5697 (98%); 1.064 (77%); 1.44; 1.771 (9%)	^{208}Pb(d,3n)^{207}Bi ^{209}Bi(p,p2n)^{207}Bi daughter^{211}At parent^{207m}Pb
^{208}Bi	3.7X10^{5}y			^{208}Pb(d,2n)^{208}Bi
		EC (100%)	Q_{EC} 2.87 (calculated)	
		γ(∿3%)	0.5100; 0.9200; 2.614 (100%) and lead X-rays	^{209}Bi(n,2n)^{208}Bi
^{208m}Bi				
$^{209}_{83}$Bi (Natural)	100% ∿10^{20}y(r)	α	3.0 (?)	σc 0.015 to ^{210}Bi σc 0.019 to ^{210m}Bi
^{210}Bi (RaE)	5.013d	α	4.681($\overset{+}{40}$); 4.644($\overset{+}{60}$)	^{209}Bi(n,γ)^{210}Bi ^{209}Bi(d,p)^{210}Bi
		β^-	1.1615 max^m(100%)	^{208}Pb(d,γ)^{210}Bi
		γ	Polonium X-ray (weak)	^{208}Pb(α,pn)^{210}Bi daughter^{210}Pb parent^{210}Po & ^{206}Tl

(+) signifies relative intensity. (r) radioactive (natural).

TABLE I. (Continued)

Isotope	Half-life or % Abundance	Type of Decay	Particle Energy (MeV)	Some Modes of Formation
^{210m}Bi	~3X10^{6}y	α(99.6%) γ	4.935($\overset{+}{6}0$); 4.89 ($\overset{+}{3}4$): 4.95 ($\overset{+}{5}$); 4.48 ($\overset{+}{0}.5$) 0.262 (45%); 0.30 (23%); 0.34; 0.61.	^{209}Bi(n,γ)^{210m}Bi parent^{210}Po&^{206}Tl
^{211}Bi (AcC)	2.16m	α(99%) γ	6.617($\overset{+}{8}3$); 6.273($\overset{+}{1}7$); 0.3507(14%); 0.405; 0.832	From uranium/actinium (4n+3) series. daughter^{211}Pb; parent^{211}Po; daughter^{215}At; parent^{207}Tl
^{212}Bi (ThC)	60.5m	α γ	5.76($\overset{+}{1}.78$); 6.043(69.7); 6.082(27.1); 0.040; 0.285; 0.33; 0.432; 0.893; 0.7271 (7%); 1.074; 1.62; & Tl X-rays	From thorium (4n) series. daughter^{212}Pb(ThB) parent^{212}Po(ThC')& ^{208}Tl(ThC'') daughter^{216}At
^{213}Bi	47m	α β^{-} γ	5.86 1.39 max^{m} 0.4370	From (4n+1) series. daughter^{217}At and ^{213}Pb parent^{213}Po&^{209}Tl
^{214}Bi (RaC)	19.7m	α(0.021%) β^{-}(99%) γ	5.507($\overset{+}{3}9.2$); 5.443($\overset{+}{5}3.9$) 3.26 max^{m} 0.6094 (47%) 0.7690; 0.9350; 1.120 (17%); 1.281; 1.416; 1.764 (17%); 2.432	From uranium (4n+2) series. daughter^{214}Pb(RaB) and ^{218}At parent^{214}Po(RaC') and ^{210}Tl(RaC'')

(+) indicates the relative intensity.

TABLE I. (Continued)

Isotope	Half-life or % Abundance	Type of Decay	Particle Energy (MeV)	Some Modes of Formation
^{215}Bi	7m	β^-	$Q_\beta \sim 2.2$(calculated)	From uranium/actinium (4n+3) series. daughter ^{219}At parent ^{215}Po

For more complete information see the following:

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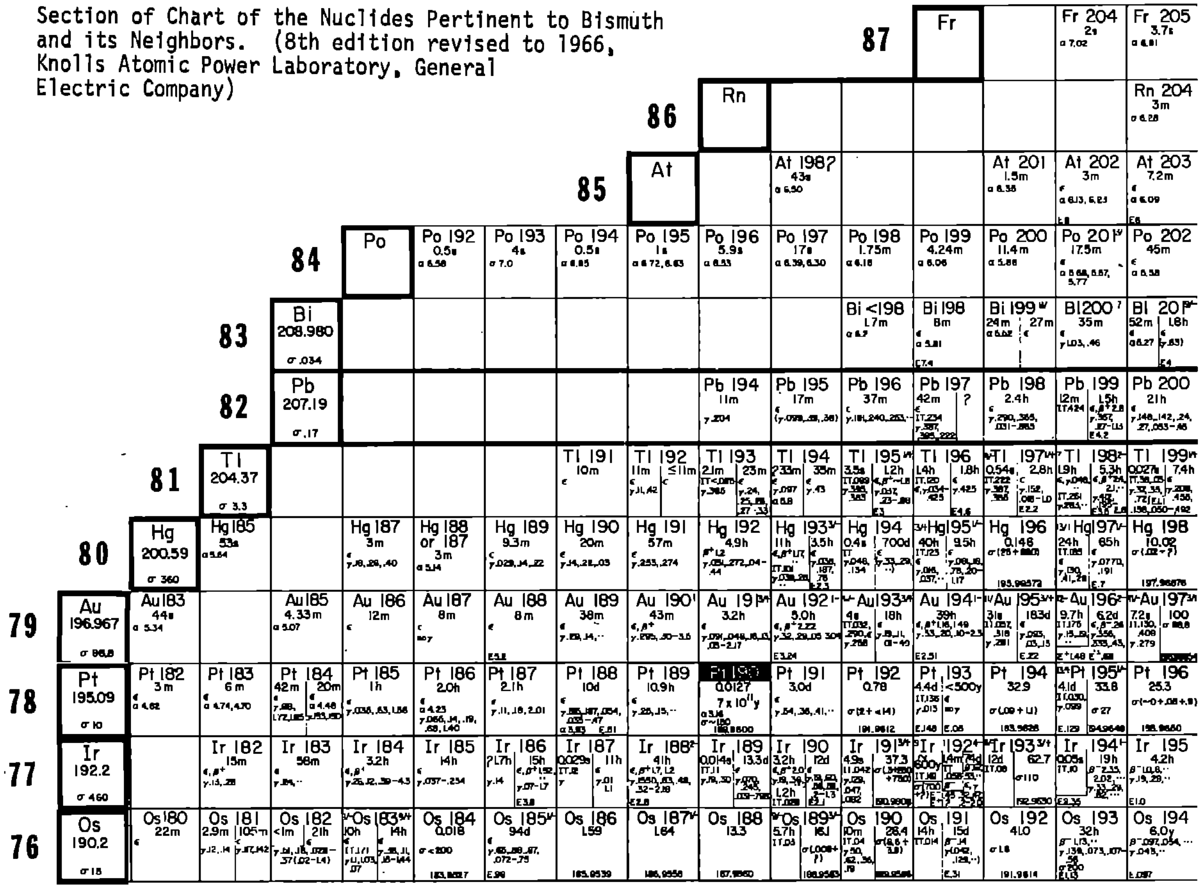
Fig. 1a.

Section of Chart of the Nuclides Pertinent to Bismuth and its Neighbors. (8th edition revised to 1966, Knolls Atomic Power Laboratory, General Electric Company)



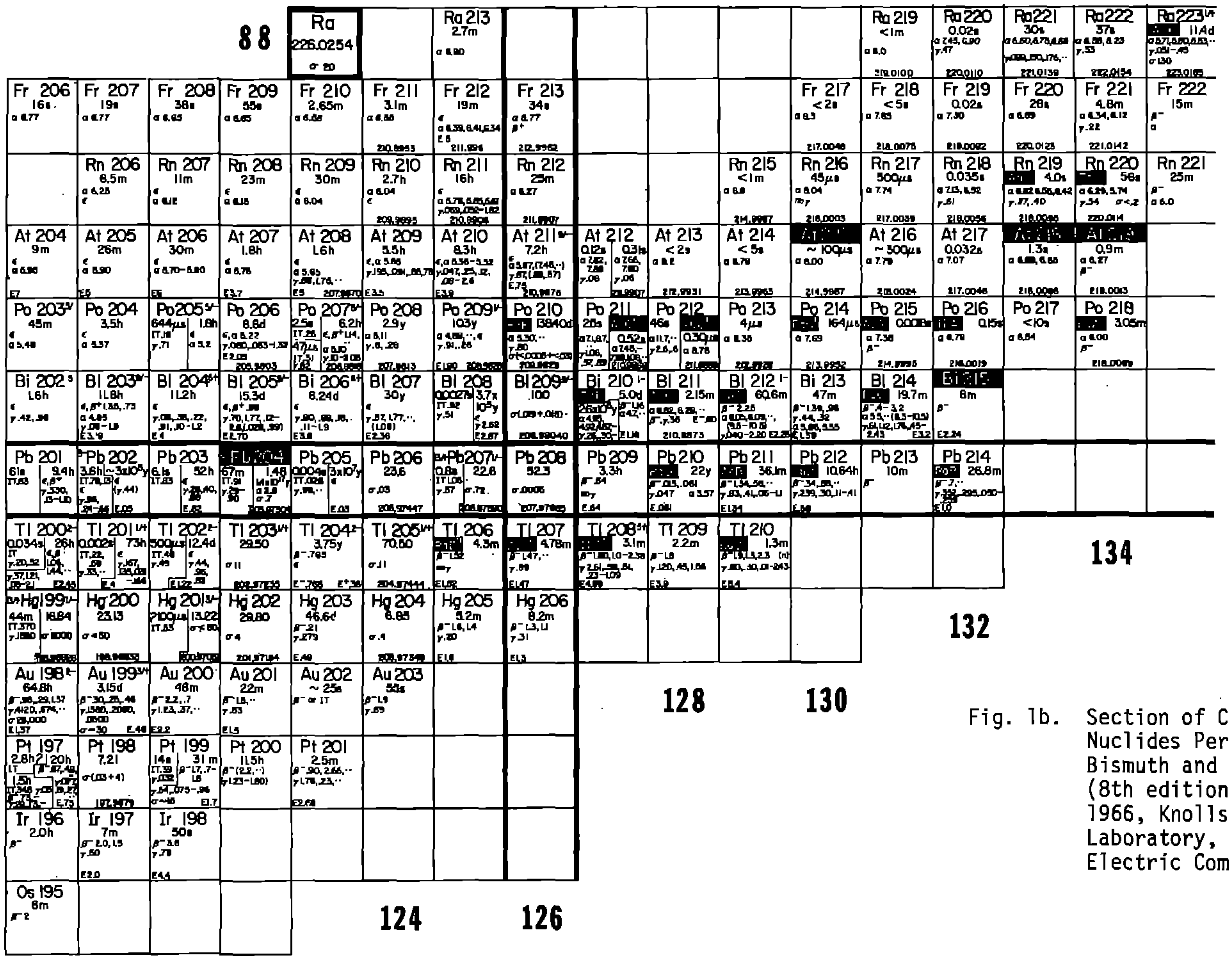


Fig. 1b. Section of Chart of the Nuclides Pertinent to Bismuth and its Neighbors. (8th edition revised to 1966, Knolls Atomic Power Laboratory, General Electric Company)

III. REVIEW OF THE CHEMISTRY OF BISMUTH

A. Metallic Bismuth

Bismuth is a brittle white metal with a pinkish tinge. It is located in Group V of the Periodic Table with nitrogen, phosphorus, arsenic and antimony. Bismuth resembles antimony in its mode of occurrence but is less common. The content of bismuth in the earth's crust has been estimated(229) to be 0.00002 weight %, about the same abundance as silver. Its cosmic abundance is estimated at about one atom per 10^7 atoms of silicon. The metallic properties of bismuth are more pronounced than that of either antimony or arsenic. The physical properties of bismuth are listed in Table II.

TABLE II.

PHYSICAL PROPERTIES OF BISMUTH METAL (339)

Atomic Number	83
Atomic Weight	208.980
Atomic Volume	21.3 cm^3/g-atom
Density (20°C)	9.8 g/ml
Crystal Structure	Rhombohedral
Melting Point	271°C
Boiling Point	1560°C
Atomic Radius	1.70 Å
Electrical Conductance	0.009 $(\text{micro-ohm})^{-1}$
Heat of Vaporization	42.7 kcal/g-atom
First Ionization Energy	185 kcal/g-atom
Specific Heat	0.034 cal/g-degree
Electro-negativity	1.9

Bismuth displays valencies of +3 and +5. In the hydride, BiH_3 bismuth has a valency of -3. The compounds of Bi(III) are the most important ones in analytical chemistry. Compounds of bismuth (IV) may also exist(50). The compounds of bismuth (V) - alkali metal bismuthates - are known only in the solid state. The ions of bismuth (V) do not exist in solution.

Because of its low absorption cross section for thermal neutrons, bismuth has attracted attention as a fuel carrier, and coolant for nuclear reactors, and as neutron windows in medical reactors.

Bismuth is one of the least toxic of the heavy metals, and cases of bismuth poisoning in industrial use have not been recorded. Therefore, toxicity is not a problem in the handling of bismuth(139). In using radioisotopes, however, health protection must be considered. For example, ^{210}Bi is considered a highly toxic and dangerous nuclide because of its long-lived, alpha-emitting daughter, ^{210}Po ($t_{1/2}$ = 134 d).

B. Chemical Properties of Bismuth

Some oxidation-reduction potentials involving bismuth are given in Table III, while chemical reactions of bismuth with several reagents are listed in Table IV.

TABLE III.

OXIDATION-REDUCTION POTENTIALS OF BISMUTH (183)

(A) in Acid Solution

$$BiH_3 \xrightarrow{\text{ca } 0.8} Bi \xrightarrow{-0.32} BiO^+ \xrightarrow{-1.59} Bi_2O_5.$$

$$Bi + 4Cl^- \rightleftharpoons BiCl_4^- + 3e^-, \ E° = -0.168.$$

$$BiOCl + 2H^+ + 3e^- \rightleftharpoons Bi + Cl^- + H_2O, \ E° = 0.1583.$$

$$Bi_2O_4 + 4H^+ + 2e^- \rightleftharpoons 2BiO^+ + 2H_2O, \ E° = 1.59.$$

(B) in Basic Solution

$$Bi + 3OH^- \rightleftharpoons BiOOH + H_2O + 3e^-, \ E_B^\circ = 0.46.$$

$$2Bi + 6OH^- \rightleftharpoons Bi_2O_3 + 3H_2O + 6e^-, \ E_B^\circ = 0.46.$$

Bismuth unites directly with sulfur and with halogens, but hydrochloric acid or hot concentrated sulfuric acid attacks it slightly. It is readily attacked by dilute and concentrated nitric acid, when the corresponding salts are formed.

Bismuth exists in aqueous solutions as Bi(III). Unless bismuth solutions are kept rather strongly acid, they are susceptible to hydrolysis, even at pH values of 1-2, forming basic salts. There is no evidence for the simple aquo ion $[Bi(H_2O)_n]^{3+}$. In neutral perchlorate solutions the main species is $(Bi_6O_6)^{6+}$ or its hydrated form $[Bi_6(OH)_{12}]^{6+}$, and at higher pH $[Bi_6O_6(OH)_3]^{3+}$ is formed(67). Bismuth hydrolysis and its effect on the extraction curve of bismuth has been studied by Stary(301). He shows that bismuth is present in aqueous solution at pH 1-2 as hydroxy cations $BiOH^{2+}$ and $Bi(OH)_2^+$ and the slope of the distribution curves equals 2 or 1 in this pH region. The hydrolysis of bismuth, lead, calcium, strontium and barium has been reviewed by Olin(238).

TABLE IV.

REACTIONS OF BISMUTH METAL WITH VARIOUS REAGENTS*

Reagent	Nature of the interaction
Nitrogen (N_2)	No reaction.
Bromine (Br_2)	Reacts on heating to form $BiBr_3$.
Water (H_2O)	No reaction at room temperature with water containing no dissolved oxygen; reacts slowly on calcination in a steam atmosphere with oxidation to Bi_2O_3.
Hydrogen (H_2)	No reaction; hydrogen is not dissolved by solid or liquid bismuth on heating to 873°K.
Air	No reaction either in dry or in wet air at room temperature; burns on heating to form Bi_2O_3.
Iodine (I_2)	Reacts on heating to form BiI_3.
Nitric acid (HNO_3)	Reacts to form $Bi(NO_3)_3$.
Sulfuric acid (H_2SO_4)	Reacts on heating with liberation of SO_2.
Hydrochloric acid (HCl)	No reaction.
Lithium (Li)	Reacts on heating to form bismuthide.
Selenium (Se)	Reacts on heating to form $BiSe_3$.
Sulfur (S)	Reacts to form Bi_2S_3.
Tellurium (Te)	Reacts to form Bi_2Te_3.
Phosphorus (P)	No reaction.
Chlorine (Cl_2)	Reacts with ignition to form $BiCl_3$.

*Data taken from Samsonov (Ref. (279) pp. 568-569).

From acid solution various hydrated crystalline salts such as $Bi(NO_3)_3 \cdot 5H_2O$; $Bi_2(SO_4)_3$ and double nitrates of the type M_3^{II} $[Bi(NO_3)_6]_2 \cdot 24H_2O$ can be obtained.

Treatment of Bi_2O_3 with nitric acid gives bismuthyl salts such as $BiO(NO_3)$ and $Bi_2O_2(OH)(NO_3)$. Similar bismuthyl salts are precipitated on dilution of strongly acid solutions of various bismuth compounds (243). These bismuthyl salts are generally insoluble in water. In solutions of Bi(III) containing excess halide ions, BiX_4^- complexes are present (67).

C. Bismuth Compounds

1. Soluble and Insoluble Salts of Bismuth, and Gravimetric Compounds

a. The Bismuth Trihalides (169, 244)

Bismuth trifluoride, BiF_3 is insoluble in water, but dissolves in concentrated hydrofluoric acid with the formation of complexes, such as $H_3(BiF_6)$. Fluorine does not easily react with bismuth even when heated; hence, BiF_3 is made by evaporating a solution of Bi_2O_3 in HF (79).

Bismuth trichloride, $BiCl_3$, dissolves in water, which hydrolyses it to BiOCl. This property is used as a test for bismuth in qualitative analysis. $BiCl_3$ dissolves in alcohol, acetone, methyl cyanide, and nitrobenzene. Bismuth trichloride solution in hydrochloric acid is reduced by hypophosphorus acid to give a dull grey powder of metallic bismuth.

Bismuth tribromide, $BiBr_3$, is generally similar to the chloride. With water it gives BiOBr. Its melting point is 217°C and boiling point is 453°C (215) (291).

Bismuth triiodide, BiI_3, crystals are black or dark brown. The compound is less soluble in water than $BiCl_3$ or $BiBr_3$.

BiI_3 is made by warming bismuth metal with iodine; by adding KI solution to $BiCl_3$; and by adding bismuth oxide to a solution of iodine in stannous chloride saturated with HCl.

b. Bismuth nitrate, $Bi(NO_3)_3$

With large excess of water, $Bi(NO_3)_3$ forms bismuth subnitrate: $Bi(NO_3)_3 + H_2O = BiONO_3 + 2HNO_3$. The $Bi(NO_3)_3$ can be prepared by the action of nitric acid on bismuth metal, or on the trioxide or carbonate.

c. Bismuthyl carbonate, $(BiO)_2CO_3 \cdot 1/2H_2O$

Bismuthyl carbonate, $(BiO)_2CO_3 \cdot 1/2H_2O$ is precipitated by addition of carbonate or bicarbonate solutions to bismuth nitrate. It loses water at 100°C, and carbon dioxide at higher temperature (79; 215)

d. Bismuth sulfate, $Bi_2(SO_4)_3$

The dihydrate and the heptahydrate of this compound are known. It can be heated fairly strongly without decomposition; but, above 400°C, it breaks down to basic salts and bismuth oxide. It is made by dissolving bismuth trioxide in concentrated sulfuric acid. It is very hygroscopic and on dilution gives various basic salts (291).

e. Oxides of Bismuth

Bismuth trioxide, Bi_2O_3, is the only well established oxide of bismuth. It has no acidic character, being insoluble in alkalis. The compound is soluble in acids and gives bismuth salts which shows that it exhibits marked basic properties. Bismuth trioxide sublimes at 1010°C, and is stable up to 1750°C. Bi_2O_3 is readily reduced to the metal when heated with carbon or hydrogen.

Bismuth suboxide, BiO is a black powder. It is said to be formed when the trioxide is reduced with carbon monoxide or when bismuth oxalate is heated. Some think that it is a mixture of Bi and Bi_2O_3 (215). The preparation and properties of Bi_2O_4 and Bi_2O_5 are described in Modern Inorganic Chemistry (Refs. 215, pp. 855 et seq., and 291)

f. Bismuthates

Bismuthates are powerful oxidizing agents in acid solution. They are, therefore, employed as oxidants in analytical chemistry. They are made (i) by heating e.g. Na_2O_2 and Bi_2O_3 giving $NaBiO_3$; (ii) by treating $Bi(OH)_3$ in strongly alkaline solution with chlorine or other stong oxidizing agents.

Gravimetric estimation of bismuth as Bi_2O_3 is normally done when the amount of bismuth is more than 5 mg. In this procedure bismuth is precipitated as basic bismuth carbonate in solution of ammonium carbonate. As bismuth carbonate is somewhat soluble in ammonium carbonate, an excess should be avoided. After digesting the bismuth carbonate precipitate on a steam bath, it is filtered, washed moderately with hot water, dried, and ignited to about 1000°C. It is finally weighed as Bi_2O_3.

In this precipitation, chlorides and sulfates which would also form insoluble basic compounds must be absent, as must also such elements or compounds as would be precipitated or cause a precipitate with bismuth in a solution containing ammonium carbonate (134).

g. Bismuth sulfide, Bi_2S_3

Bismuth trisulfide is isomorphous with antimony trisulfide, and has a similar structure (291).

Bismuth sulfide, Bi_2S_3, is very insoluble; precipitation of bismuth as the sulfide is quantitative even from very strongly acid solution, e.g., up to 18-N H_2SO_4. A separation of bismuth from cadmium can be effected in this way.

h. Bismuth phosphate, $BiPO_4$

Bismuth phosphate, $BiPO_4$, is a white heavy, crystalline precipitate which is quite insoluble in water and in dilute nitric acid. It is so stable upon ignition that it can be dried above 119°C, and its weight is constant even at 961°C (80).

This property of bismuth phosphate has been used in estimating macro amounts of bismuth as $BiPO_4$. In the absence of interfering elements, quantities of bismuth up to 500 mg can be determined with an accuracy of 0.2% (79, 134, 215, 319).

The solubility of bismuth phosphate in 0.1-N nitric acid is approximately 0.1 mg/ℓ at 30°C. In the presence of excess phosphate the solubility is negligible. However, since the solubility increases rapidly with increasing acidity, the acidity must be less than 0.5 N, and preferably as low as 0.1 N (319).

2. The Bismuthyl Compounds

The action of water on any of the bismuth trihalides or on the nitrate,sulfate, or perchlorate of bismuth produces insoluble bismuthyl precipitates. These precipitates (except the perchlorate) are non-hygroscopic. They can be heated to red heat before they decompose (291).

a. Bismuthyl chloride, or bismuth oxychloride, BiOCl

Bismuthyl chloride differs from the oxychloride of arsenic and antimony in that it is not decomposed by water, and from antimony oxychloride in being insoluble in tartaric acid (215). It dissolves only in warm fused tartaric acid (79).

This property of bismuth chloride to give an insoluble precipitate of BiOCl has been used to develop a gravimetric procedure. It is normally employed when only a few milligrams of bismuth are involved, preferably less than 5 mg.

The procedure is usually carried out by neutralizing a nitric-acid solution of bismuth with NH_4OH, adding a few drops of HCl, and diluting considerably with water. The precipitate of BiOCl is then digested on a steam bath. Elements such as Ag, Hg(I) and Tl that form insoluble chlorides, elements such as Sb, Sn, and Zr that are easily hydrolyzed, and compounds such as sulfates, phosphates, and arsenates that form insoluble precipitates with bismuth must be absent. The precipitate of BiOCl can be washed well with hot water, then with alcohol and dried to constant weight at 100°C.

The properties of other bismuth compounds such as BiOBr, BiOI, etc. are given in Table V, page 19.

3. Organic Compounds of Bismuth

a. Bismuth 8-hydroxyquinolinate (Bismuth Oxinate)

A typical chelating precipitant, 8-hydroxyquinoline, also referred to as 8-quinolinol or oxine, is one of the best known and the most versatile organic reagents. The literature pertaining to the use of this reagent is extensive, but is well summarized in numerous monographs (136; 224; 333). The reagent is not very selective and precipitates almost every simple metal ion with the exception of the alkali metals. However, the selectivity of oxine precipitation can be increased by the use of masking agents such as EDTA, tartrate, etc.

That bismuth oxinate can be extracted from aqueous solution by a suitable organic solvent such as chloroform at a lower pH value of about 4 can be used as a preliminary step to separate bismuth from cadmium, cobalt, nickel and zinc, etc. in the course of its gravimetric and volumetric analyses.

Bismuth may be precipitated by oxine either as an orange-yellow, crystalline precipitate of $Bi(C_9H_6ON)_3 \cdot H_2O$ from acetic acid or ammoniacal tartrate solution free from halides (95), or as $C_9H_7ON \cdot HBiI_4$ from acidic solutions. The former precipitate may be weighed after drying at 105°C. After long heating at 130-140°C, the precipitate becomes anhydrous.

b. Bismuth pyrogallate

Pyrogallol has been used for the detection of at least 23 elements and in the determination of half that number (89).

Pyrogallol reacts with bismuth salts in nitric acid solution ($\leq$ 0.1 N) to form an orange-yellow precipitate. This reaction has been used for the detection and determination of bismuth (Ref. 333, pages 162 and 163). By means of this reaction 71 μg of bismuth in one ml of solution have been detected.

Bismuth pyrogallate precipitated from 0.1-N HNO_3 solutions can be dried at 110°C and weighed. This method has been used to separate bismuth from cadmium, copper, lead and zinc. Ostroumov (240), who studied various methods for the determination of bismuth in the presence of lead and copper, reports that the pyrogallol method is one of the three best ones that he has tested.

c. Bismuth Phenylarsonate

Phenylarsonic acid precipitates bismuth quantitatively at pH 5.1 to 5.3 as the basic salt $C_6H_5AsO_3BiOH$, from solutions buffered with sodium or ammonium acetate. Lead interference is prevented if the concentration of ammonium acetate is kept high.

The basic bismuth phenylarsonate may be dried and weighed or dissolved in HCl and analyzed iodometrically. For further details on the determination of bismuth in the presence and in the absence of interfering ions see Majumdar (200) and Flagg (95).

d. Bismuth Salicylaldoximate

With salicylaldoxime Bismuth gives a bright yellow precipitate, which is quantitative between pH 7.2 to 9.4 or higher. This precipitate, which is approximately represented by the formula $(C_7H_5O_2N)BiOH$, contains 57.3 per cent bismuth. As the precipitate is not definite in composition, and since it cannot be obtained in a weighable form, the most suitable procedure is to ignite the complex to Bi_2O_3 before weighing for determining bismuth. If the pH is adjusted to 9 bismuth can be separated from silver. The separation from zinc can be achieved if the alkalinity is adjusted to a pH of 10 (65; 302).

e. Bismuth Thionalate

The reagent can be used for precipitation of most of the elements which normally precipitate from acid solution with hydrogen sulfide (95). Many members of this hydrogen sulfide group can be prevented from precipitating by addition of suitable masking agents.

This makes the reagent more specific than the normal hydrogen sulfide treatment. Antimony, bismuth, gold, lead, thallium and tin, for example, are precipitated from carbonate solution containing tartrate and cyanide, while from strongly alkaline solution containing these ions only thallium is precipitated. However, unlike the sulfides the thionalates have definite compositions, and many of the salts may be weighed after drying at moderate temperatures (95).

Bismuth can be precipitated quantitatively from acid solution by thionalide. It can be separated from aluminum, arsenic, cadmium, chromium, cobalt, copper, iridium, mercury, nickel, palladium, platinum, silver, titanium, vanadium and zinc by precipitating it from an alkaline solution containing tartrate and cyanide.

The bismuth-thionalate complex, $Bi(C_{12}H_{10}ONS)_3$ can be dried at 100°C to constant weight. It contains 23.87% bismuth. For details about the determination of bismuth from acid as well as tartrate cyanide solution see Flagg (Ref. 95, pages 276-77).

f. Miscellaneous organic precipitants

Bismuth is quantitatively precipitated with benzenearsonic acid as $BiC_6H_6AsO_4$ from an acetic acid solution buffered with sodium acetate or ammonium acetate, at pH 5.1-5.3. In the presence of KCN, bismuth can be separated by this reagent from silver, copper, cadmium, cobalt, nickel, mercury and lead (200).

In the presence of NaOH glucose reduces bismuth salt solution to metallic bismuth. (89) This precipitated bismuth metal can be weighed.

The reaction of mercaptophenylthiothiodiazolone (or "Bismuthiol II") with solutions of bismuth salts can be used for the gravimetric and colorimetric estimation of bismuth. The composition of the compound obtained by heating to 105°C corresponds to the formula $Bi(C_8H_5N_2S_3)_3 \cdot 1\text{-}1/2H_2O$. Though many of the heavy metals interfere, the results obtained by this method are claimed to be excellent (200).

4. Summary of the Properties of Bismuth Compounds

On the following pages useful data on important compounds of bismuth have been summarized. Table V lists physical properties of Bi(III) compounds, while Table VI includes information on the solubilities of Bi(III) compounds in water and other solvents.

TABLE V.

PHYSICAL PROPERTIES OF BISMUTH (III) COMPOUNDS

Compound	Formula weight	Color and Crystalline Form	Density	M.P. °C.	B.P. °C.	Solubility
$BiAsO_4$	347.91	Monoclinic	7.142			Slightly soluble in cold water, very slightly in acid.
$BiBr_3$	448.75	Yellow	5.604	218	453	Soluble in HBr, Ethyl ether.
$Bi_2O_3 \cdot CO_2 \cdot H_2O$	528.03	White-powder	6.86	decomp.		Soluble in acid.
$BiCl_2$	279.91	Black Needles	4.86	163	decomp. 300	
$BiCl_3$	315.37	White crystals	4.75	230	447	Soluble in alcohol.
$BiC_6H_5O_7$	398.11	Colorless crystals		decomp.		Soluble in NH_4OH. Insoluble in alcohol.
$(BiO)_2Cr_2O_7$	666.02	Orange red				Soluble in acid. Insoluble in alkali.
BiF_3	266.00	Gray powder	5.32			Decomposes in acid.
$Bi(OH)_3$	260.02	White amorphous	4.36	$-H_2O$, 100	-1-1/2 H_2O 150	Soluble in acid. Insoluble in alkali.
$Bi(IO_3)_3$	733.73	White				Slightly soluble in HNO_3.
BiI_3	589.73	Dark hexagonal	5.64	439	500 decomp.	Soluble in HI, KI.
$Bi(NO_3)_3 5H_2O$	485.10	Colorless triclinic	2.82	decomp. 30°	$-5H_2O$ 80	Soluble in acid. Insoluble in alcohol.
$BiONO_3 \cdot H_2O$	305.02	Hexagonal plates	4.928	decomp. 260°		Soluble in acid.
$Bi_2(C_2O_4)_3$	682.07	White powder				Soluble in acid.
Bi_2O_3	466.00	Yellow, rhombic	8.9	820	1900	Soluble in acid.

TABLE V. (Continued)

Compound	Formula weight	Color and Crystalline Form	Density	M.P. °C.	B.P. °C.	Solubility
Bi_2O_3	466.00	Yellow,tetragonal	8.55	860		Soluble in acid.
Bi_2O_3	466.00	Yellow, cubic	8.20	704		Soluble in acid.
$Bi_2O_4 \cdot 2H_2O$	518.03	Brown yellow	5.6	decomp. 100	-0;305	Soluble in acid.
Bi_2O_5	498.00	Brown	5.10	-0;1.50	-20; 357	Soluble in acid. KOH
$Bi_2O_5 \cdot H_2O$	516.02	Red	5.75	$-H_2O$ 120	-20; 357	Soluble in acid. KOH.
BiOBr	304.92	Colorless, crystalline	8.08	decomp.		Soluble in acid. Insoluble in alcohol.
BiOCl	260.46	White	7.72			Slightly soluble in H_2O, Soluble in acid, insoluble in acetone, NH_3, $H_2C_4H_4O_6$.
BiOF	244.00	White, crystalline	7.5	decomp.		Soluble in acid.
BiOI	351.91	Red, rhombic	7.92	decomp.		Soluble in acid. Insoluble in KI, alcohol.
$BiPO_4$	303.98	White, monoclinic	6.323	decomp.		Slightly soluble in hot H_2O, soluble in HCl. Insoluble in dil. HNO_3.
Bi_2Se_3	654.88	Black, rhombic	6.82	710	decomp.	Insoluble in alkali.
$Bi_2(SO_4)_3$	706.20	White needle	5.08	decomp. 418		Soluble in acid.
Bi_2S_3	514.20	Brown, rhombic	7.00	685 decomp.		Soluble in HNO_3.
Bi_2Te_3	800.83		7.7	573		Decomp. in HNO_3, insoluble in con. HCl, H_2SO_4.

TABLE VI.

SOLUBILITIES OF BISMUTH (III) COMPOUNDS IN WATER AND VARIOUS OTHER SOLVENTS (303)

Compound		Temp. °C.	Solubility in water g/l	Solubility in other solvents g/l
Name	Formula			
1. Ammonium citrate	$Bi_2(NH_4)_2(C_6H_5O_7)_3$	25	222.5	13.4 in 51% ethanol
2. Chloride, tri-	$BiCl_3$	--	Decomposes	Soluble in ethanol
		18	--	152 in acetone; 16.3 in ethyl acetate
		20	--	320 in hydrazine
3. Citrate	$BiC_6H_5O_7$	25	0.10	Soluble in NH_4OH; 0.41 in 50% ethanol
4. Hydroxide	BiOOH	20	1.44×10^{-3}	--
	$Bi(OH)_3$ ($-H_2O$ at 100°C)			Soluble in acids; insoluble in alkali
5. Iodate	$Bi(IO_3)_3$	--	Insoluble	Slightly soluble in nitric acid
6. Iodide	BiI_3	--	Insoluble in cold; decomposes in hot	Soluble in HI and in KI
		20	--	35 in absolute alcohol
7. Lactate	$BiC_6H_9O_6 \cdot 7H_2O$	25	126	--
	Anhydrous	25	16	--

TABLE VI. (Continued)

Compound		Temp. °C.	Solubility in water g/l	Solubility in other solvents g/l
Name	Formula			
8. Nitrate	$Bi(NO_3)_3 \cdot 5H_2O$ ($-5H_2O$ at 80°C)	19	--	294.3 in acetone (303) 420 in acetone (182)
		25	286 (anhydrous)	Soluble in acid; insoluble in alcohol
9. Nitroso-β-phenyl-Hydroxylamine	$Bi(C_6H_5N_2O_2)_3$	18	4×10^{-4}	--
10. Oxalate	$Bi_2(C_2O_4)_3$	20	Insoluble	3×10^{-3} in HNO_3 (∿0.5N) 12.7×10^{-2} in HNO_3 (∿4N)
11. Phosphate, ortho-	$BiPO_4$	--	Very slightly soluble	Soluble in HCl, but insoluble in dilute HNO_3
12. Salicylate (basic)	$BiC_7H_5O_3$	20	0.10	1.60 in ethanol
13. Selenide	Bi_2Se_3	--	Insoluble	Insoluble in alkali
14. Telluride	Bi_2Te_3	--	--	Insoluble in cold HCl or H_2SO_4; decomposes in HNO_3

D. Precipitation and Coprecipitation

1. Coprecipitation of Bismuth

Coprecipitation is important not only as a means of concentrating or separating materials, but also as a tool in expanding knowledge of the mechanism of precipitation and the properties of solid solutions (186; 328).

In the case of radioactive substances, the concentration of radionuclides in solution is frequently so low that addition of a precipitant does not cause the solubility product of the nuclide compound to be exceeded. However, if what is termed a "carrier" substance is present in the solution, precipitation of this "carrier" will often bring down the desired nuclide. A variant of this method involves the adsorption of the nuclide compound from aqueous solution on preformed precipitates. An example of coprecipitation technique is the precipitation of plutonium in trace quantities on lanthanum trifluoride or bismuth phosphate.

a. Coprecipitation with Hydroxides of Iron and Aluminum

The coprecipitation of bismuth on ferric hydroxide or aluminum hydroxide is a useful preliminary separation step, provided large quantities of metals which precipitate as insoluble hydroxides in ammoniacal solution are absent (134).

Coprecipitation of bismuth with ferric hydroxide has been applied to a separation of ^{207}Bi from a cyclotron irradiated lead target (86). Deuteron irradiation of lead target resulted in the formation of ^{205}Bi ($t_{1/2}$ = 14.5d) and ^{206}Bi ($t_{1/2}$ = 6.4d), in addition to ^{207}Bi ($t_{1/2}$ = 30y). After dissolving the copper-lead alloy target in nitric acid, the bismuth activities were coprecipitated on iron hydroxide using pyridine as a precipitant (86). One additional precipitation gave bismuth activities free from all the other impurities, except some traces of lead. Further separation by anion exchange gave a bismuth-207 solution which contained only 2 to 3 μg/ml of lead with a bismuth yield of about 99%.

Ferric hydroxide precipitation has also been employed (3) for separation of bismuth from molybdenum concentrates. The best pH range for such a precipitation has been reported as 6.5 to 8.0. The yield of bismuth recovered was one hundred per cent.

Traces of bismuth in uranium have been separated by carbonate in the presence of hydroxides of iron and aluminum.

Bismuthyl hydroxide, BiOOH may be precipitated and its solubility is recorded (183) as 5.8 x 10^{-6} M. If one were justified in assuming complete ionization into hydroxide and bismuthyl ions, the solubility product would be 3.3 x 10^{-11}.

b. Coprecipitation with Sulfides of Copper, Cadmium, etc.

Bismuth belongs to the second group in qualitative analysis, where elements are precipitated as sulfides by passing H_2S gas into the solution under study.

Elements Bi, Cd, Cu, Pb, Hg, Ag etc., whose sulfides are insoluble in acids and in solutions of alkali sulfides, are in subgroup A. The solubilities of various sulfides in water are tabulated in Lange (182).

Lavrukhina (185) studied systematically the coprecipitation behavior of radioactive isotopes of bismuth, zirconium, cerium and iodine with sulfides and hydroxides of various metals. He concluded that the coprecipitation of radioactive nuclides with hydroxides and sulfides of various elements does not depend on the solubility of the latter; thus, coprecipitation of ^{210}Bi equals 98-100% with hydroxides, e.g., $Fe(OH)_3$ (where molar solubility S = 3.4 x 10^{-10} M) and with $Fe(OH)_2$ (S = 1.3 x 10^{-5} M). It is also quantitatively precipitated with sulfides, namely, HgS (S = 6 x 10^{-27} M) or CdS (S = 3 x 10^{-14} M).

Copper sulfide has been used for separation of bismuth impurity in preparation of niobium (346); thioacetamide was used as a precipitant. A similar preconcentration method was employed for separation of bismuth and other trace impurities in other metallurgical materials (16) before they were determined spectrochemically. Cadmium sulfide was employed as a coprecipitating agent by Chuiko (61) and by Ziegler (353).

c. Coprecipitation on Other Substances

As little as 0.7 μg of Bi(III) was determined (348) by adhesion on a glass surface. Wolf, *et al.* (344) used a mercury oxide column to adsorb ^{210}Bi in order to separate it from the uranium - radium decay chain.

In the determination of trace amounts of bismuth in lead, a preliminary separation of bismuth by coprecipitation on mercurous chloride was used by Pribil and Cuta (256).

2. Precipitation of Bismuth

a. Inorganic Precipitants

Bismuth forms important oxyhalides like BiOCl, BiOBr and BiOI, which are insoluble in water. They are precipitated when solutions of Bi^{3+} in concentrated acids are diluted. Antimony also shows a similar behavior.

Precipitation of bismuth as the oxyhalide is one of the most widely employed methods for the separation and isolation of bismuth (100). The precipitate is formed by adding dilute HCl or HBr to a solution of $Bi(NO_3)_3$ or $Bi(ClO_4)_3$ that is just acidic enough to keep the solution clear; this solution is then boiled after further dilution with water. Bismuthyl iodide (BiOI) has also been used (223) for the same purpose. The basic nitrate separation is effected by repeated evaporation to dryness of a nitric acid solution or by Luff's method (215), in which ammonia and sodium nitrites are added to a solution of bismuth salts, then neutralized to incipient precipitation by ammonia. Luff also mentions a basic sulfate separation.

Other metals such as antimony, tin, zirconium etc. which hydrolyze readily, or metals such as silver which form insoluble halides, interfere in the determination of bismuth as bismuthyl salts.

Precipitation of bismuth sulfide from dilute HCl is an important group separation for bismuth but a host of other elements of the second group of qualitative analysis are also precipitated with bismuth. The solubility product of bismuth sulfide for the reaction $Bi_2S_3 = 2Bi^{3+} + 3S^{2-}$ as reported by Kolthoff (170) is $K = 1.6 \times 10^{-72}$.

The treatment of the sulfide precipitate with ammonium sulfide dissolves the sulfides of As, Sb, Sn, Mo, Se, Te, Re and Ge. Sulfides of Au, Ir and Pt dissolve either entirely or partially, as stated previously. This dissolution of sulfides is due to the formation of complex thio salts. Knox (164) established that bismuth, though insoluble in sulfide solution containing only the hydrosulfide ion SH^-, is soluble in solutions containing the sulfide ion, S^{2-}. Thus, bismuth sulfide *dissolves* in solutions of alkali sulfides, and in mixtures of alkali sulfides and hydroxides, the solubility increases with increasing concentration of alkali hydroxide. However, unlike the arsenic group (IIB) ammonium sulfide, alkali hydrosulfides and alkali hydroxides (in absence of sulfides) *do not dissolve* bismuth sulfide.

Scott and Furman (105) precipitated bismuth sulfide directly with a solution of potassium hydrosulfide. But bismuth precipitates obtained with H_2S are usually not pure, and the precipitation is not very quantitative. This difficulty was overcome by Taimni and Salaria (316) by adding ammonium sulfide to a solution of bismuth at a pH just acidic enough to keep the solution clear. In this way they obtained a pure Bi_2S_3 precipitate. The precipitate can be washed with hot water, dried and weighed as Bi_2S_3 (316). Bismuth is also quantitatively precipitated in the range of 15 to 280 mg from homogeneous phases by slow hydrolysis of thioacetamide (96; 115; 306) to produce sulfide ions; thus, $CH_3CSNH_2 + H_2O = CH_3CONH_2 + H_2S$. This method has been employed to precipitate the major quantity of bismuth in uranium-bismuth alloys prior to the determination of uranium (306). The sulfide precipitation is considered to be the best approach (51) for preconcentrating bismuth and other trace elements in Rotor Steels.

A separation of bismuth from cadmium (both II A group elements) can be effected (160) by precipitating bismuth sulfide from a fairly strong sulfuric acid solution (up to 18 N). In the separation of thallium and bismuth, from sulfuric acid medium the increase in the ratio of Tl:Bi from 5:10 to 5:100 caused an increase in the precipitation of Bi_2S_3. Hydrochloric acid medium was found best for such a separation (35).

Sulfuric acid medium was used by Tananayev *et al.* (318) for precipitating bismuth and zirconium employing disodium phosphate, tagged with phosphorus-32, as precipitant. A dense, crystalline precipitate of bismuth phosphate is obtained from a hot, acid solution. Using a specially prepared ammonium phosphate solution (293), a quantitative precipitation of bismuth was obtained from a dilute HNO_3 solution of pH 0.6. This method is used to determine bismuth in pure bismuth-lead, eutectic alloy.

The phosphate method is a good method for separating bismuth from aluminum and from most divalent metals. Thorium, zirconium, hafnium, titanium and other metals that form highly insoluble phosphates interfere (100).

Bismuth is frequently associated with lead; therefore, a separation of bismuth and lead is quite important. An interesting method of selective separation of bismuth from lead and several other metals is described by Pribil and Cuta (256). In this method, the acidic sample solution is treated with EDTA to complex bismuth and other metals, and the solution is then made basic with NH_4OH. The addition of excess calcium salt now takes the EDTA away from the bismuth and thus causes bismuth hydroxide to precipitate. Lead and several other metals in the sample remain complexed by the EDTA and do not precipitate.

Good results for the bismuth-lead separation by a double precipitation as the basic formate were reported by Ostroumov (240) and others (193, 335). This method was originally proposed by Benkert and Smith (26) and was modified by Kallmann (154) to obtain a sharp separation of bismuth from lead.

Clark's method (63) was used by Schoeller and Waterhouse in which bismuth was precipitated as the metal by heating the acid solution with a piece of steel wire. Bismuth is also reduced to the metal in Evans' hydrosulphite separation (87) or by hypophosphorous acid from perchloric acid (42). Formaldehyde also reduces bismuth to metal. Alkali and alkaline-earth metals, Al, Cr, Co, Fe, Pb, Mg, Mn, Ni or Zn do not interfere.

Bismuth, copper, nickel, palladium and antimony are precipitated quantitatively at a pH of 2.0 by sodium borohydride (83). The cobalticyanide ion also precipitates bismuth quantitatively from sulfuric acid solution (∿25 vol %), even in the presence of small quantities of Na_2SO_4. But, no precipitation occurs in HCl media and only partial precipitation in HNO_3. This method separates bismuth from tin and antimony but not from Cd, Cu, Ag, Mn, Fe, V and Zn, these latter elements are also precipitated (88).

Tin, arsenic and antimony, which frequently are present in bismuth samples, are removed by volatilization of their bromides in perchloric acid (25).

Willard and Goodspeed (338) separated lead and bismuth by taking advantage of the fact that lead nitrate is insoluble in concentrated HNO_3, whereas bismuth nitrate is soluble.

The separation of bismuth from mercury involves the treatment of the mixed sulfide precipitate with hot dilute HNO_3 in which bismuth sulfide is soluble, but mercuric sulfide is not (223).

b. Organic Precipitants

The precipitation of bismuth with cupferron was first used by Pinkus and Dernies (248). Cupferron precipitates bismuth quantitatively from a 1-M solution of HCl or HNO_3. In acid solution bismuth can be separated from other elements, for instance, Pb and Cd, which precipitate in neutral media. This method has been used (45) in concentrating bismuth from alloys containing lead and other elements before spectrographic analysis. Copper, iron and tetravalent metals get precipitated with bismuth by cupferron under these conditions. But, it separates bismuth from a large number of elements such as Al, Sb, As, Cr, Co, Mn, Hg, Ni, Zn, Ag, and alkali metals in addition to Cd and Pb.

The lower pH limit for the quantitative precipitation of bismuth with 8-quinolinol (oxine) is 5.2. It is quantitative between pH 5.2 and 10.5. Bismuth has been determined in the presence of magnesium within the pH range 5.2-5.4, using a strong acetate buffer (130). Bismuth precipitation by oxine has also been described by Beard (23) in his report on the radiochemistry of antimony and bismuth.

Milligram quantities of bismuth have been determined to an accuracy of one percent (9, 133) by precipitating it as a 8-hydroxy-quinoline-tetra-iodo-bismuthate complex $[(C_9H_7ON)\ HBiI_4]$. This precipitation was studied (262) by using iodide lablelled with ^{131}I. The loss of activity from the solution used up in the bismuth precipitation gave a measure of the amount of bismuth originally present in the sample.

Quantitative precipitation of bismuth is obtained with thionalide in 0.1-N acid solution. If chloride or sulfate is also present, the acid concentration may be raised to 0.2 N. Several other members of the acid H_2S group also precipitate with bismuth. Employing cyanide and tartrate as masking agents bismuth is quantitatively precipitated from a moderately alkaline solution by thionalide and thus separated from Al, As, Cd, Cr, Co, Cu, Fe, Hg, Ni, Pd, Pt, Ag, Ti and Zn (100).

A selective precipitation of bismuth by dimethyl glyoxime from an alkaline solution of pH 11.0 to 11.5 containing EDTA and CN^- as masking agents was obtained by Vitek and Lott (323). They separated 50-500 mg of bismuth from various amounts of Al, As, Ba, Cu, Cd, Co, Cu, Pb, Mn, Hg, Ni, Pd, Pt, Ag, Sr, W and Zn.

Phenylarsonic acid and its derivatives as precipitating agents for bismuth and various other metallic ions were studied by Nakata *et al.* (230). In the presence of KCN, phenylarsonic acid separates bismuth from Cd, Co, Cu, Pb, Hg, Ni and Ag (100); Al, Be, Fe, Ti, and U constitute important interferences.

Abrao (1) employed bismuthiol (2,5-dimercapto-1, 3,4-thiodiazole) for separation of ^{212}Pb, ^{212}Bi, and ^{212}Po from solutions of thorium nitrate. His method consisted of the addition of bismuthiol to the nitrate solution and the subsequent filtration or centrifugation of the precipitate. The advantage in the recrystallization of the reagent prior to its use as the precipitant and the use of mercury or copper as collectors for these radio-nuclides from thorium nitrate solution is discussed (1).

A method of isolating radioactive bismuth from metallic lead and its compounds and from radium by precipitating bismuth as n-propyl gallate has been described (161). This bismuth-lead separation was achieved in a quantitative manner by acidic dissolution of 10 to 20 g of lead, adding about 10 mg of bismuth carrier in the nitrate form, and precipitating bismuth with an n-propyl gallate solution in 0.01-N HNO_3 at the boiling point. The yellow crystalline precipitate of bismuth is dried to constant weight at 110°C and weighed as $C_{10}H_9O_5Bi \cdot H_2O$. Propyl gallate has also been employed as a gravimetric reagent for bismuth and antimony (341).

Bismuth is separated from Pb at pH 2.25 by selective precipitation as bismuth gallate. Lead is then determined in the filtrate as gallate at pH 6.25 (329). Separation of bismuth from cadmium and copper and its determination as gallate is also described (217).

E. Bismuth Complex Ions and Chelates

Bismuth (III) forms complexes with a variety of ligands. Useful data on complexes with inorganic ligands are included in Table VII, and with organic ligands in Table VIII.

F. Analytical Determinations other than Gravimetric

The determination of the yields of constituents of a mixture can always be useful, allowing simple and fast group separations to be performed from complex mixtures of radioelements followed by measurement of the groups without further separation, by gamma-ray spectral analysis using NaI(Tl) or Ge(Li) detector systems, or gamma and beta particle decay analysis.

Various methods for the determination of bismuth have been tabulated by Templeton and Bassett (319).

1. Volumetric Methods

Numerous procedures for the volumetric determination of

TABLE VII. STABILITY CONSTANTS OF SOME BISMUTH(III) COMPLEXES WITH INORGANIC LIGANDS

Name	Ligand Formula	Method*	Temp. °C	Medium	Equation	Log of Equilibrium Constant
Arsenate	AsO_4^{3-}	sol, gl	20	var		-9.36 (K_{so})
					H	11.54 (K_1); 6.77 (K_{12}); 2.25 (K_{13}).
Halides (mixed & comparative)		sp		4NaX, 1HClO$_4$	$BiCl_5^{2-}$ - (Br^- - Cl^-)	1.23 (K_1); 0.77 (K_2); 0.52 (K_3K_4); -0.5 (K_4); 0.26(K_5)
		sp	25	dioxane	$BiICl_2+BiI_3 \rightleftarrows 2BiI_2Cl$	-0.8 (K).
					$BiCl_3+BiI_2Cl \rightleftarrows 2BiICl_2$	0.56 (K) in dioxane(I).
Nitrate	NO_3^-	sol	25	0 corr	$BiONO_3(s)+2H^+ \rightleftarrows Bi^{3+} + NO_3^- + H_2O$	-2.55 (K_{so})
		sol	25	var		-2.18 (K_{so}); 1.26 (K_1)
Perchlorate	ClO_4^-	cfu	25	1NaClO$_4$	ev $Bi_6O_6L_2^{4+}$	
		oth	25	1(Na,H)ClO$_4$	ev $Bi_6O_6L_2^{4+}$	
Thiosulphate	$S_2O_3^-$	sp		2.7CH$_3$CO$_2$H	ev BiL_3^{3-} & BiL_5^{7-} of BiL_6^{9-}	
		var		var	ev BiL_3^{3-}	3.32 (β_3).

*sol = solubility; sp = spectrophotometry; gl = glass electrode; cfu = centrifuge or ultracentrifuge; var = various methods; oth = other methods.

TABLE VIII. STABILITY CONSTANTS OF BISMUTH(III) COMPLEXES WITH ORGANIC LIGANDS

Name	Ligand Formula	Method*	Temp. °C	Medium	Equation	Log of Equilibrium Constant
Citric acid	$C_6H_8O_7$	pol				β_2 14 - 18
2,3-dihydroxy-butane dioicacid (tartaric acid)	$C_4H_6O_6$	dis	20	0.1($KClO_4$)		β_2 11.3 ± 0.1
Ethanedioic acid (oxalic acid)	$C_2H_2O_4$	dis	20	0.1($KClO_4$)		K_{so} - 35.4
Nitritotriacetic acid	$C_6H_9O_6N$	gl	25	0.1(KNO_3)	$BiL+H_2A^- \rightleftarrows BiLHA^{3-} + H^+$	K - 1.80
					$BiLHA^{3-} \rightleftarrows BiLA^{4-} + H^+$	K - 3.84
4-(2-Pyridylazo)	$C_{11}H_9O_2N_3$	sp			$Bi^{3+}+HL^- \rightleftarrows BiHL^{2+}$	K - 18.2

*pol = polarography; dis = distribution between two phases; gl = glass electrode; sp = spectrophotometry.

bismuth have been suggested, but many of these are indirect and are based on the precipitation reactions of bismuth compounds (223). Some are given below briefly:

a. Methods Based on Precipitation Reactions

Potassium chromate method

Potassium chromate, K_2CrO_4 is generally used volumetrically, but gravimetric and colorimetric procedures are also possible. In the usual method bismuth solution (0.005 N) is poured into a mixture of 5 ml of 0.1-M sodium acetate and 5 ml of 0.03-N potassium chromate. After 5 minutes the entire mixture is diluted to 50 ml with water. The solution is filtered, and to a 25-ml aliquot of the filtrate is added 100-200 mg of KI and 5 ml of 6-N sulfuric acid. After 10 min it is titrated with 0.005-N sodium thiosulfate solution (168).

Potassium iodate, KIO_3, can be similarly employed instead of K_2CrO_4.

Potassium Ferrocyanide Method

Potassium ferrocyanide, $K_4Fe(CN)_6$ permits direct titration. To the bismuth solution containing 5-70 mg of bismuth in dilute H_2SO_4 (pH ~ 1.6) is added 1 to 5 ml of 0.1-M KI as indicator, 2 to 10 ml glycerol, and the mixture is diluted to 50 ml with water. This is titrated with a 0.05-M solution of $K_4Fe(CN)_6$.

Oxalic Acid-Permanganate Method

In this method bismuth is precipitated with oxalic acid from dilute HNO_3 solution, and the precipitate, after proper treatment, is titrated with 0.1-N $KMnO_4$ solution. Lead, Ag, Cu, Fe, Zn and Te do not interfere (105).

b. Methods Based on the Reduction of Bismuth Metal

Since bismuth can exist only in the zero and +3 oxidation states, the possibilities for oxidation-reduction titrations are very limited. In spite of this, the reduction to metal has been made the basis of several titrimetric methods (223).

Busev (47) has successfully titrated bismuth(III) to the free metal with a standard chromium solution. He carried out the titration under CO_2 in 0.6 to 6-M HCl. This makes bismuth determination possible in the presence of lead and cadmium.

When a hydrochloric acid solution of bismuth is boiled with metallic copper, bismuth is precipitated, and an equivalent amount of cuprous chloride appears in solution which can be titrated with potassium bromate (223).

c. Miscellaneous Methods

Other methods employing $K_3Cr(SCN)_6$, $Na_2S_2O_3$, sodium arsenate, and molybdate etc. have been described elsewhere (105; 168; 324) and will not be discussed here.

Moser (227) made a systematic study of some of these methods and an oxalate procedure in which bismuth sulfide was digested with a solution of ferric salt. The resulting ferrous ions were then titrated with permanganate. He concluded that of all the methods tested by him (in 1907), the molybdate method was the best (223; 227).

d. Complexometric Titrations Using EDTA

During the last fifteen years or so, the formation of stable metal-complex ions, by titration of metal-ion solutions with a standard solution of a complexing agent, has become increasingly important as a method of volumetric analysis.

The most important complexing agent which has been extensively studied is ethylenediaminetetraacetic acid (abbreviated as EDTA) (285; 334) and its disodium salt. These compounds are sometimes called by common names such as Trilon B, Complexone III, Sequestrene, Versene and Chelaton 3. Other complexing agents (complexones) which are sometimes employed include nitrilotriacetic acid (NTA, NITA, or Complexone I), and 1,2-diaminocyclohexane-N, N, N', N'-tetra-acetic acid (DCTA, DCYTA, or Complexone IV).

The best-known chelating agent, studied in greatest detail, and with the widest general application is EDTA. This is because of its relatively low price, and the spatial structure of its anion, which has six ligand atoms which correspond to the coordination number most frequently encountered among the metals; in addition, it forms strainless five-membered rings on chelation. In other cases, it behaves as a quinquedentate or quadridentate ligand, having one or two of its carboxyl groups free of strong interaction with the metal ion.

The abbreviation, H_4Y is the usual representation for EDTA, which behaves as a tetraprotic acid; the disodium salt is Na_2H_2Y and affords the complex-forming ion H_2Y^{2-} in aqueous solution. Y^{4-} is used to represent the ethylenediamine tetraacetate ion.

The stability of a complex is characterized by the stability constant or the formation constant K, (the reciprocal of this is called the dissociation constant or the instability constant). A number of formation or stability constants of metal chelates are given in summary form in the Handbook of Analytical Chemistry (213). More extensive data are available in the compilation of Martell and Sillen (209). The first two replaceable hydrogen atoms of EDTA (H_4Y) are moderately strong acids, with acid dissociation constants $pK_1 = 1.99$ and $pK_2 = 2.67$, much stronger than normal carboxylic acids. On titration of EDTA with NaOH, the two carboxyl groups are neutralized first; then, further addition of base removes the hydrogen atoms on the ammonium groups ($pK_3 = 6.16$, and $pK_4 = 10.26$). These values of acid dissociation constants can be used to calculate the distribution of EDTA species at any particular pH. Thus, at pH > 12 most of the EDTA exists as the tetraanion Y^{4-}; around pH 8 the predominant species is HY^{3-}; while a solution containing mainly H_2Y^{2-} ions has a pH of 4.4. Most metal EDTA titrations are, therefore, performed in neutral or alkaline solutions where the predominant species are H_2Y^{2-} and HY^{3-}.

In a titration, protons and metal ions compete for the reactive chelating ion, and the net reaction may be visualized as

$$M^{n+} = H_2Y^{2-} \rightleftharpoons MY^{(n-4)+} + 2H^+$$

or

$$M^{n+} + HY^{3-} \rightleftharpoons MY^{(n-4)+} + H^+$$

depending on the exact pH of the solution (279) (334).

The protons liberated in these reactions could change the pH sufficiently to cause a significant amount of back reaction, i.e., metal complex dissociation in the presence of acid. To prevent this, the titration systems are usually buffered with an excess of an innocuous buffer. Maintaining a constant pH assists detection of the end point since the change in pM (i.e., -log [M]) at the equivalence point remains similar from assay to assay.

Therefore, some discrimination among various groups of metals can be achieved by proper control of pH. In acid solutions of pH 1 to 3, for example, tri- and quadrivalent cations can be titrated without interference from divalent cations. At pH ~5, all divalent cations except those of the alkaline earths are titratable. The alkaline earth elements are also titratable, if the titration is carried out at pH 10.

These divisions are related to the differences in stability constants of the complexes. For Bi^{3+}, Fe^{3+}, Ga^{3+}, In^{3+}, Co^{3+}, Sc^{3+} and Th^{4+} etc. the value of log K is greater than 20. For lanthanides, aluminum, and divalent transition elements, such as Fe^{2+}, Co^{2+}, Ni^{2+} etc., log K is between 14 and 18; however, log K is 8 to 11 for the alkaline earths.

Much greater selectivity than that obtained by control of pH can be achieved by using *masking* agents, either to prevent interference by unwanted cations or to displace a cation from its EDTA complex, followed by back titration of the liberated EDTA. A wide range of such masking agents is available (97; 213; 245; 334) from which to form, with particular cations, complexes that are very stable, preferably soluble and colorless, inactive towards EDTA, and also not reactive toward the indicators that are employed in these titrations. Difficulties arise when cations have low probabilities of forming complexes, or when they give rise to intensely colored complexes. The use of masking and demasking agents permits the successive titration of many metals (285).

Indicators in EDTA Titrations

The success of an EDTA titration depends on the precise determination of the end point. The most common procedure utilizes metal ion indicators. Numerous organic compounds have been proposed for use as metal ion indicators in EDTA titrations. Some of them are Eriochrome Black T, Eriochrome Blue-Black B, Eriochrome Red B, Murexide, Fast Sulphon Black F, Xylenol Orange, Pyrocatechol Violet, Bromopyrogallol Red, Calmagite, etc. (324).

Types of Titrations with EDTA

The most important procedures for the titration of metal ions with EDTA are

Direct titration, in which the metal ion is directly titrated with a standard EDTA solution, after buffering the system to the desired pH. The end point can also be determined by methods other than visual, such as spectrophotometry, amperometry, etc.

Back-titration, where an excess of standard EDTA solution is added to the metal solution and the resulting solution is buffered to the desired pH, the excess of the EDTA is then back titrated with a standard metal ion solution.

Substitution, or replacement titration (285; 334).

Bismuth Determination with EDTA Titrations

In the case of bismuth both the "direct" and the "back" titrations can be performed with EDTA. Using methyl-thymol blue, pyrocatechol violet or xylenol orange as indicators, the direct complexometric titration of bismuth is achieved in the pH range 1-3. The main interference in this type of titration comes from tri- and tetravalent cations.

Standard EDTA Solutions

Ethylenediaminetetraacetic acid is insoluble in water but the disodium dihydrogen salt is soluble. The disodium salt is marketed as the dihydrate and is available in analytical reagent purity commercially. This can be used as a primary standard for titrimetric work. In solution, the disodium salt is almost completely dissociated according to the reaction

$$Na_2H_2Y \rightleftarrows H_2Y^{2-} + 2Na^+$$

Thus, a solution of the disodium salt is, in effect, a solution of the ion H_2Y^{2-}. This is the solution generally referred to as "EDTA". It may be weighed out directly as the dihydrate after drying at 80°C, as the commercial analytical reagent grade may contain traces of moisture. An EDTA solution of 0.1-M concentration contains 37.225 g of the reagent per liter. As an additional check, the EDTA solution may be standardized by titration with zinc solution (324).

Commercial EDTA may be purified by the method given in Kodama (168), Vogel (324), or Welcher (334).

Polythene bottles are the most satisfactory containers (324), and should always be employed for the storage of very dilute (e.g., 0.001 M) solution of EDTA.

Some typical methods employed in the determination of bismuth by EDTA titration are given below.

Using Bromopyrogallol Red as Indicator

A known aliquot (25 ml) of bismuth solution (∿0.01 M) is diluted to 100 ml with distilled water. The pH of the solution is adjusted to between 2 and 3 by the cautious addition of ammonia, and about 20 drops of the indicator solution (0.05% in 50% ethanol) are added. Titration is then carried out with standard EDTA solution (0.01 M)until the color changes from claret red to yellow-orange.

Here, 1 ml of 0.01-M EDTA ≡ 2.09 mg of Bi.

Using Xylenol Orange as Indicator

The procedure is similar to (i), but here only 3 or 4 drops of the (0.5%) indicator solution are added. At the end point the color changes sharply from red to orange-yellow. In this titration if both the solutions are 0.05 M, then

1 ml 0.05-M EDTA ≡ 10.45 mg Bi.

Using Pyrocatechol Violet as Indicator

Here, the initial dilution of bismuth solution is to 50 ml, pH 2.5 to 3.5 and the indicator solution is 0.1% in water; 3 to 5 drops of indicator are employed. Titration is continued until color changes from blue to yellow. A violet transition color may develop just before the end point, but this changes sharply to yellow at the equivalence point.

Using Methyl Thymol Blue Indicator

Again, the indicator solution is 0.1% in water, but the color change is from yellow to blue. Bismuth is titrated in acidic solution.

Using Thiourea as Indicator

With 0.5 to 0.8 g of indicator at pH ∿ 2.0, 30-80 mg of bismuth have been determined, employing 0.05-M EDTA solution (168). Thiourea also helps in masking copper.

Masking Agents in Bismuth Titrations with EDTA

Iron and mercury, if present, can be reduced by ascorbic acid, and their interference in bismuth titration can be prevented. Mercury can also be masked with KCNS, and subsequent demasking is achieved by the addition of $AgNO_3$. In the complexometric titration of bismuth, thorium can be masked by sulfate. In addition to mercury, silver, and platinum metals, KCN prevents interference by copper, nickel, cobalt and iron, Triethanolamine also masks iron(III). Tirron masks aluminum and titanium, while KI masks mercury.

Fritz (99) added fluoride to prevent the interference by beryllium and certain of the lanthanides. He added tartaric acid to prevent interference from antimony. Cadmium can be masked with phenanthroline when the titrations are carried out at pH 5 - 5.5.

Back titration of bismuth with EDTA becomes necessary when it is to be determined in the presence of cadmium, lead, and indium. The back titration is done in the pH range 5 - 5.5 with zinc, using methylthymol blue as indicator. This gives the total content of the mixture. The titration is then repeated in the presence of mercaptoacetic acid as a masking agent for bismuth, so that the amount of bismuth present can be obtained by difference (245). The sum of bismuth and indium can be found by back titration at pH 2.2 - 2.5 of an excess of EDTA, using standard bismuth solution. Back titration with manganese in ammoniacal solution, in the presence of ascorbic acid and cyanide to mask bismuth and cadmium, gives total lead plus indium (258).

When a bismuth titration is carried out in acidic medium (pH 1-3), lead, zinc, and cadmium do not interfere.

From ammoniacal solution, in the presence of EDTA and KCN, bismuth can be precipitated as diethyldithiocarbamate complex, and separated from cadmium, lead and indium. The bismuth carbamate complex can be extracted into chloroform. Bismuth is then recovered from the organic extract by treatment with HNO_3 (220).

Another method of removing bismuth from various other cations in these titrations is to precipitate it as BiOCl by hydrolyzing the bismuth chloride solution.

Other masking agents for bismuth in EDTA titrations include 2,3-dimercaptopropanol (BAL), dithiol, mercapto succinate. Citrate ion can also be used if only small amounts of bismuth are present (245; 271).

2. Colorimetric and Spectrophotometric Methods

Colorimetry is well suited to the determination of small concentrations of ions. As little as 10^{-5} per cent of a constituent can be determined, whereas it is difficult — and generally inaccurate — to go below 0.01% by methods of volumetric or gravimetric analysis.

Colorimetric determinations have been used occasionally in the past by radiochemists (109). In terms of sensitivity, convenience, selectivity and precision, spectrophotometric methods are generally superior to comparative colorimetry and even to photoelectric colorimetry, where only broad band filters are employed to filter white light (27; 52). Also, spectrophotometric determinations are less subjective and are well adapted to both routine and occasional analysis (58; 134). Therefore, in spite of the higher cost of spectrophotometric equipment, this method is recommended and is the one primarily considered in this review.

A standard bismuth solution for colorimetry is prepared by dissolving 100 mg of pure bismuth in either 20 ml of concentrated H_2SO_4 or HNO_3 and diluting to one liter with water. One ml of this standard solution contains 0.1 mg bismuth. Other standard solutions may be obtained by dilution.

a. Dithizone Method

Dithizone (see page 51), dinaphthylthiocarbazone, and their numerous derivatives form intensely colored compounds with bismuth ions. These compounds are extractable with chloroform and with other organic solvents (46; 281).

Dithizone (diphenylthiocarbazone) is the outstanding reagent for the colorimetric determination of traces of bismuth. This reagent has attained prominence in bismuth chemistry due not only to the sensitivity of the determination (less than 10 μg of Bi can be determined), but also to the selectivity with which the bismuth dithizonate can be extracted into organic solvents such as chloroform or carbon tetrachloride.

The wavelength used for the determination of bismuth dithizonate is around 500 nm, and the minimum in the dithizone absorption occurs very close to this wavelength, at 510 nm. On the other hand, bismuth dithizonate absorbs very little at 620 nm, where the strongest absorption is shown by the dithizone itself in the organic solvent. Therefore, the amount of bismuth can be measured precisely by the absorption of light by the bismuth dithizonate at 510 nm, or by the absorption of light by the excess of dithizone remaining after the reaction is complete at 620 nm. Another frequently employed procedure is to measure the intensity of the excess dithizone absorption at 620 nm; then the measurements of the bismuth complex at 510 nm are corrected for contributions due to excess dithizone.

The colorimetric determination is achieved by extracting bismuth from an acidic medium (pH 1 to 4) into a solution of dithizone in $CHCl_3$ or CCl_4, and observing the extinction of the organic extract at 505 nm when $CHCl_3$ is employed or at 490 nm with CCl_4. In acidic medium (pH ∿2.0), bismuth forms an orange-yellow, primary bismuth dithizonate, but in basic medium (pH ∿9), an orange-red complex is formed. These complexes are extractable with organic solvents such

such as $CHCl_3$ or CCl_4.

In the absence of interfering elements the colorimetric determination of bismuth is done as follows: Adjust the acidity of the bismuth solution, containing 0 to 50 μg of bismuth in 50 ml of solution, to a pH between 1 and 3. Add to it 15 ml of dithizone solution in chloroform (60 mg of dithizone per liter of redistilled chloroform) and shake the mixture for about one minute. Place a small plug of cotton in the tip of the stem of the separatory funnel and run about 5 ml of the organic layer through it. Discard this chloroform and fill the cell of the spectrophotometer or a photoelectric colorimeter with the filtered chloroform solution. Find the absorbance of the solution at 505 nm (or better, at 510 nm). This procedure is called a mixed-color method. An additional reading may be taken of the same solution at 620 nm to determine the unused portion of the reagent, dithizone, and its corresponding correction to be applied at 505 nm (or at 510 nm). (Fischer, cited in ref. 281). Also see pp. 51-53 of this monograph.

Complete extraction of bismuth is also possible from weakly alkaline citrate solution. The presence of cyanide, which prevents extraction of most other metals that interfere with the determination of bismuth, does not affect the extraction of bismuth, as cyanide does not complex bismuth strongly. For other details see Sandell (281), who has described the dithizone system quite elegantly.

Plots showing percentages of bismuth extracted at various values of pH with different amounts of excess dithizone are given by Greenleaf (cited in 150). Bouissieres and Ferradini (44) reported that the extraction of bismuth-210 (RaE) was about 80% when 1-M HNO_3 was employed. The dithizone solution in chloroform was 100 mg of H_2Dz per liter. But, under similar conditions, less than 5% bismuth was extracted, when 1-M HCl was employed. This distinctly proves the formation of stable bismuth chloro-complexes. Much chloride also hinders the extraction at higher pH.

In the presence of cyanide, bismuth can be separated from Cu, Ag, Cd, Zn, etc. Lead, Tl(I), and Sn(II) also react with dithizone in basic cyanide solution. Lead is the only metal which gives difficulties in the separation of bismuth, as tin does not react in the stannic state and thallium can be separated more easily than lead, e.g., by complexing with pyrophosphate (281). When the primary problem is to separate bismuth from much lead, cupferron extraction is more suitable than dithizone extraction. Bode and Heinrich (40) have shown that, by successive extractions with chloroform solutions of cupferron, bismuth can be removed quantitatively from 0.1-M HNO_3 solution: It is also reported (281) that precipitation of bismuth cupferrate in the pH range 0.5-1.5 effects a separation of bismuth from both lead and cadmium (see also page 53).

If bismuth is present as a trace element in other matrices which do not precipitate on treatment with H_2S, it can be coprecipitated with copper or cadmium carrier as the sulfide from homogeneous solution with thioacetamide (312). The separation of bismuth from copper or cadmium can then be achieved as described earlier by dithizone extraction. It is also best to isolate bismuth as the sulfide, when it is to be determined in the presence of much calcium and phosphorus, as in samples of bone.

Bismuth can be back extracted from the carbon tetrachloride phase by shaking the latter with 0.2% HNO_3 containing bromide.

b. Thiourea Method

Thiourea, $CS(NH_2)_2$ reacts with bismuth ions in HNO_3 or H_2SO_4 solutions to form an intense yellow coloration (46; 281), which is suitable for colorimetric determination of bismuth, especially when the amount of bismuth is larger than 1 mg. The absorption maxima are at 322 nm and 470 nm, and a fourfold sensitivity is obtained in the ultra violet region, where the absorbancy conforms to Beer's law for 0.6-6 ppm of bismuth (297). The concentration of thiourea is also important in the bismuth determination.

The thiourea method, though somewhat less sensitive than other colorimetric methods for bismuth (such as dithizone and potassium iodide methods), is widely used because of its excellent selectivity (100).

Cadmium, Cu, Hg, Ag and Sn form a white precipitate with thiourea when present in high concentration, but they do not interfere in moderate amounts. The precipitate obtained by these elements with the reagent can be filtered off and bismuth determined in the filtrate. Adequate amount of thiourea reagent should be added to take care of these interfering elements.

Antimony(III) forms a weak yellow complex with thiourea and can be complexed with 0.5% citric acid. Antimony not removed in the lead separation can also be complexed with tartaric acid and sodium fluoride (297). Fluoride destroys the antimony-thiourea color but does not affect the bismuth complex.

Interference from tin and antimony can also be removed by volatilizing them as bromides prior to the colorimetric estimation of bismuth. Iron in excess of 0.1 mg per 50 ml must be removed or reduced to the ferrous state by ascorbic acid or with hydrazine sulfate.

Serious interference occurs when traces of bismuth are to be determined in the presence of large amounts of lead. In such cases bismuth can be separated by precipitation with thionalide (95). Bismuth can also be separated from the bulk lead by precipitation of lead chloride. Selenium and tellurium interfere.

Yoe and Overholser (cited in 281, p. 337) found that some substituted thioureas gave slightly more sensitive reactions with bismuth than thiourea itself. Benzidine-dithiourea gives a sensitivity about four times as great as that given by thiourea. Makukha (cited in 281) states that di-o-tolyl-thiourea is ten times as sensitive as thiourea. Bhatki (28) and Bhatki and Kabadi (31; 32) used 2,naphthyl thiourea for the colorimetric determination of bismuth using a photoelectric colorimeter.

c. Potassium Iodide Method

When potassium iodide solution is added to a dilute H_2SO_4 solution containing a small amount of bismuth, a yellow to orange coloration, due to the formation of an iodobismuthate ion, is produced. The color intensity increases with iodide concentration up to about 1% KI and then remains practically constant. Small amounts of bismuth in the range 0.05-0.5 mg can be determined by this method. The actual procedure is as follows:

Adjust the sample to contain 0.3-3 mg of bismuth per 100 ml in 1-2 N H_2SO_4. Mix 10 ml of sample, 10 ml of H_2SO_4 ($\sim$29 N) and 20 ml of 14% KI and 1% ascorbic acid. Dilute to 50 ml with water and read at 337 nm against a reagent blank. This reading of the orange-yellow color in the ultraviolet gives much more sensitivity than reading in the visible at 460 nm.

Among the interfering substances should be mentioned are copper and trivalent iron that react to give iodine, certain members of the arsenic group that give colored solutions, and colored salts such as nickel nitrate, in sufficient concentrations to tint the solution. Thallium(I) and lead in large amounts precipitate with KI and badly occlude bismuth (100). These can be removed by the usual separations or by treatment to fit the case in question (134).

Oosting (cited in 281 and 297) reported a superior extraction procedure for bismuth based on the formation of a brucinium iodobismuthite complex soluble in chloroform. Quantities of bismuth of the order of 100 µg can be determinted satisfactorily by reading at 425 nm in the presence of up to 5 mg of Ag, Al, As, Cr, Fe(III), Mn, Ni and Zn. Bismuth at the 50 µg level can be determined in the presence of as much as 250 mg of lead and 500 mg of copper, if these are complexed with cyanide and EDTA, and if the bismuth is extracted with diethyldithiocarbamate (DEDTC). After evaporating the chloroform used for the extraction of the diethyldithiocarbamate complex, the DEDTC acid is decomposed rapidly by treatment with 2-N H_2SO_4, and bismuth is determined as brucinium iodobismuthite complex.

d. Comments on These Three Colorimetric Methods

The dithizone method is recommended when 10 µg or less of bismuth is to be determined, because its sensitivity is so great that even 1 µg of bismuth can be determined with fair precision. For amounts greater than 10 µg the iodide method will frequently be satisfactory. But, when iodide is used as a reagent, a reducing environment must be maintained to prevent liberation of iodine by air oxidation. On the other hand, thiourea provides a sensitivity almost as good as that of iodide and has the advantage of permitting the presence of relatively large amounts of lead and small amounts of copper and silver. Dithizone has one drawback compared to iodide method, in that it requires the separation of bismuth from other heavy metals, particularly lead, which react in much the same manner as bismuth; however, iodide can be applied directly in the presence of small amounts of lead as well as other metals such as iron (281).

e. Other Colorimetric Reagents

Sodium-diethyldithiocarbamate permits determination of 0-300 µg of bismuth from EDTA and cyanide solutions, in the presence of other metals. The bismuth complex can be extracted into carbon tetrachloride at pH 11-12, and measured at 370 nm ($CHCl_3$) or 400 nm (CCl_4) within 30 min. Large amounts of mercury or copper interfere at 370 nm. Ammonium tartrate is added, if much antimony or beryllium is present. It also prevents hydroxide precipitation. Other interferences are avoided by adding suitable complexing agents. A procedure which permits the determination of 0.1 mg or less of bismuth in the presence of 1 mg each of Hg(II), Cd, Ag, 5 mg Cu(II), and 100 mg Pb has been described (281). When absorbance is measured at 400 nm the sensitivity is about half that of the iodide method.

In the colorimetric determination of bismuth with diethylammonium diethyldithiocarbamate, the bismuth is extracted by chloroform from 3-N H_2SO_4 solution. This method separates bismuth from lead and ferrous iron (see p.57).

Bismuth can be removed quantitatively from 0.1-M HNO_3 solution by successive extractions with cupferron in chloroform. In the presence of tin and antimony, bismuth can be extracted by cupferron, if tartaric acid is also present to keep them complexed. For metals which precipitate with cupferron from 0.1-N acid, enough cupferron should be added to provide an excess. This is an excellent method for separation of bismuth from lead (281).

Rubeanic acid-silicotungstic acid reagent gives, with bismuth solution in dilute HNO_3, a brown coloration on heating, suitable for 0.02-0.2 mg bismuth. The color intensity obeys Beer's law and is shown to be sensitive to 0.02 mg of bismuth. No interference is observed from Al, As, Cr, Fe, Mg, Mn, alkalis, and alkaline earths.

The bismuth complex with EDTA absorbs in the ultraviolet at 263.5 nm. To a bismuth solution at pH 0.8-1.2 containing 2-25 ppm bismuth is added a solution of 0.001-M EDTA, and the color is measured at 263.5 nm (see Fig. 2). Lead, copper, iron, mercury, tin, antimony and nitrate interfere. The peak at 263.5 nm is applicable over the range of pH 2-9 (297).

3. <u>2-Pyridylazo Compounds</u>

1-(2-Pyridylazo)-2-naphthol (PAN), or β-PAN, and 4-(2-Pyridylazo) resorcinol (PAR) have proved to be most versatile reagents for metals. About fifty 2-pyridylazo reagents have been extensively studied, but only a few have so far found their way into actual analytical practice (290).

The replacement of the 2-naphthol group of PAN by resorcinol yields PAR. In contrast to PAN, PAR and its metal complexes are water-soluble, offering advantages as chromogenic agents and metal indicators in aqueous media.

PAN forms intensely colored, water-insoluble complexes with many metals. The complexes can be extracted into various solvents, including chloroform, benzene, carbon tetrachloride, 1-pentanol, and ether, and are soluble in water-miscible solvents such as acetone, ethanol, and dioxane. The metal-PAN complexes are mostly red (290), and their colors in various solvents have been tabulated in Ref. 290. PAN commonly forms chelates with metal to ligand molar ratios of 1:1 and 1:2. Metals that give either a color reaction or a

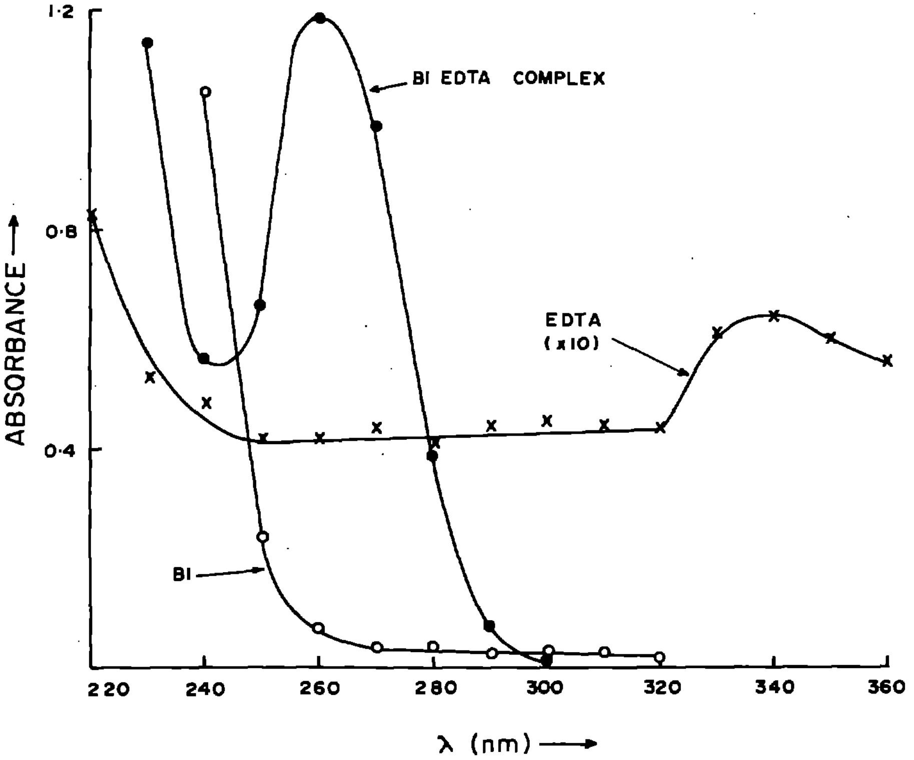


Fig. 2 Absorption spectra of Bi EDTA complex, bismuth, and EDTA solutions in the ultraviolet region.

precipitate with PAN are Bi, Cd, Co, Cu, Fe(III), Ga, Hg, In, Ir(IV), Mn, Nb(V), Ni, Pb, Pd, Pt(IV), Rh(III), Sb(III), Sn(II), Tl(III), Th, UO_2(II) and Zn. Data on the influence of various masking agents on the reactions of metal ions with PAN in aqueous media are summarized in Ref. 290.

It is seen from the data given by Shibata (290) that in the presence of EDTA, only UO_2^{2+} reacts with PAN, and all other elements are masked. In the presence of fluoride and citrate, only Cd(II), Co(II), Hg(III), In, Mn(II), Ni, and Zn give positive tests with PAN; however, PAN reacts with Bi, Ce(III), In, La, Mn(II), Pb, U, and Y in the presence of cyanide.

Very sensitive tests for the detection of various metal ions have been developed by Fujimoto and Iwamoto (104), based on the reaction of PAN with the ion after its sorption on a few beads of an appropriate ion exchange resin (Dowex 50W or Dowex 1).

Synthesis of PAN, PAR and other similar reagents have been described elsewhere. Those interested in this type of reagents should refer to the excellent review by Shibata (290).

PAN is normally used as a 0.1% solution in ethanol. This solution can be stored for a long time without change. The reagent can also be prepared in an organic solvent for extraction.

PAR forms a red-colored complex with bismuth, which is extractable into tributyl phosphate (TBP) from 0.1-0.28-M nitric acid (320). Color reactions of PAR with various metal ions in acid, basic, and neutral solutions are also given in a table of Ref. 290.

G. Solvent Extraction

Solvent extraction, or liquid-liquid extraction, occupies a very important position among the separation methods in radiochemical analysis because of its simplicity, speed, wide applicability, and relatively small contamination hazards (145; 224). Solvent extraction procedures developed for macro-concentrations are in most cases applicable to trace or even carrier-free concentrations of radioactive nuclides (221).

Most elements form extractable complexes under certain conditions (224), (301). Various organic chelating agents, such as cupferron, dithizone, oxine (8-quinolinol), dimethylglyoxime, sodium diethyldithiocarbamate, thenoyltrifluoroacetone, etc., as well as organic solvents themselves (e.g. either, acetylacetone, etc.) play very important roles in the formation of the extractable chemical species of the metals of interest (57; 71; 162).

The proper adjustment of acidity of the aqueous phase and the use of masking agents improve the selectivity of the extraction methods. Masking agents prevent the extraction of certain elements into the organic phase by forming strong water soluble (usually negatively charged) complexes of the elements (56; 245). Great strides along this line have been made in the past several years, particularly in the analytical determination of various inorganic ions (119; 145; 246; 301).

TABLE IX. COLOR REACTIONS OF VARIOUS 2-PYRIDYLAZO COMPOUNDS WITH BISMUTH

Reagent[a]	Color	Lowest pH or range[b]	λ maximum, nm
PAN; β-PAN	Pink		
P-PAN	Blue	2	
5-bromo-p-PAN	Blue	2	
3,5-dibromo-p-PAN	Green	2	
p-MP-PAN	-	2.65	
PAR	Red	0-3.5	515, 530
MPPAR	Red	1.3-3.0	520-530
PAC	Violet	3-3.5	
5-bromo-PAC	Violet	0.65-1	390
3,5-dibromo-PAC	Blue	0.65-1	400
EAPAC	Violet	3-3.5	560
5-bromo-EAPAC	Dark red	1.5-2	570
3,5-dibromo-EAPAC	Violet	0.65-1	580
DEPAP	Violet	1.5-2	
5-bromo-DEPAP	Violet	1-1.5	590
5-iodo-DEPAP	Dark red	0.65-1.0	590
3,5-dibromo-DEPAP	Violet	0.65-1.0	600
PADNS	Pale Violet	0-2.5 with nitric acid	
PAOx	Red Violet	1.5-2	
5-methyl-PAOx	Violet	-	

[a] Explanation of reagent abbreviation is given in a footnote to Table X.

[b] The lowest pH at which a significant coloration is observed. The relative sensitivity for ions has been reported (290) to be PAN > PAR > PADNS > PAOx > PACh > PA-H.

[c] Extracting solvent was 1-pentanol.

TABLE X. SOME PHYSICO-CHEMICAL DATA FOR THE BISMUTH COMPLEXES OF VARIOUS 2-PYRIDYLAZO REAGENTS[a]

Reagent[b]	λ max, nm	Molar adsorptivity, ε at maximum, liters/mole-cm	M:L molar ratio	pH (in ethanol)	Stability constant
3,5-Dibromo-PAC	400	1.2×10^4		2	
5-Bromo-PAC	390	1.3×10^4		2	
DEPAP	570	3.8×10^4	1 : 1	2	6.3×10^5
EAPAC	560	4.35×10^4	1 : 1	4.2	0.5×10^2
5-Bromo-EAPAC	570	4.6×10^4	1 : 1	2	1.09×10^6
3,5-Dibromo-EAPAC	580	5.2×10^4	1 : 1	2	2.8×10^5
5-Bromo-DEPAP	590	5.8×10^4	1 : 1	2	4.6×10^5
5-Iodo-DEPAP	590	6.1×10^4	1 : 1	2	7.4×10^5
3,5-Dibromo-DEPAP	600	6.6×10^4	1 : 1	2	1.5×10^5

[a] From ref. 123.

[b] Explanation of reagent abbreviations:

PAN, β-PAN, 1-(2-pyridylazo)-2-napthol; p-PAN, 4-(2-pyridylazo)-1-napthol; 5-bromo-p-PAN, 4-((5-Bromo-2-pyridyl)azo)-1-naphtol; 3,5-dibromo-p-PAN, 4-((3,5-dibromo-2-pyridyl)azo)-1-naphthol; p-MPPAN, 4-(3-(1-Methyl-2-piperidyl)-2-pyridyl)azo)-1-naphthol; PAR, 4-(2-pyridylazo) resorcinol; MPPAR, 4-((3-(1-methyl-2-piperidyl)-2-pyridyl)azo) resorcinol; PAC, 2-(2-pyridylazo)-p-cresol; 5-bromo-PAC, 2-((-5-5-bromo-2-pyridyl)azo)-p-cresol; 3,5-dibromo-PAC, 2((3,5-dibromo-2-pyridyl)azo)-cresol; EAPAC, 5-(ethylamino)-2-(2-pyridylazo)-p-cresol; 5-bromo-EAPAC, 2-((5-bromo-2-pyridyl)azo)-5-(ethylamino)-p-cresol; 3,5-dibromo-EAPAC, 2-((3,5-dibromo-2-pyridyl)azo)-5(ethylamino)-p-cresol; DEPAP, 5-(diethylamino)-2-(2-pyridyl-azo)-phenol; 5-bromo-DEPAP, 2((5-bromo-2-pyridyl)azo)-5-(diethylamino) phenol; 5-iodo-DEPAP, 5-(diethylamino)-2((5-iodo-2-pyridyl)azo) phenol; 3,5-dibromo-DEPAP, 2-((3,5-dibromo-2-pyridyl)azo)-5-(diethylamino) phenol; PADNS, 6,7-dihydroxy-5-(2-pyridylazo)-2-napthalene-sulfonic acid; PAOx, 7-(2-pyridylazo)-8-quinolinol; 5-methyl-PAOx, 5-methyl-7-(2-pyridylazo)-8-quinolinol.

The classification of extraction systems described in the following pages is adopted from Morrison and Freiser (224; 226).

1. Ion Association Systems

a. Halide System

It is possible to separate bismuth from tantalum and niobium in aqueous HF solutions by extracting the latter elements with methyl isobutyl ketone (219). Iofa and Vysotskii (143) succeeded in extracting carrier-free ^{210}Bi from HCl solutions with n-butyl alcohol. Extraction of bismuth from aqueous iodide solutions by ethyl ether is never more than 35% complete, but it is claimed that methyl isobutyl or methyl isopropyl ketone extracts Bi quantitatively (337).

b. Thiocyanate System

This system seems useful to remove major active species such as Fe(III), Sn(IV), Mo(VI) etc. from bismuth (37). An interesting three phase extraction study using diantipyrilmethane as the solvent was made by Russian workers (352), who found that some of the trace elements that can be concentrated simultaneously with Bi are Mo, W, Sn, Zn, Co, Fe, Cu, Ga, In, Ti, Zr, U, Hg, and Cd.

c. Nitrate System

Employing a saturated $Al(NO_3)_3$ solution, Th, Bi and Po can be quantitatively separated from Pb and Ra with mesityl oxide (204). A rapid separation of Po, Bi and Pb from At has been described (22).

Various organic solvents were examined in an attempt to develop a method for the separation of Bi and Po. Dibutyl carbitol was found to be a good extracting agent for the removal of traces of Po from large amounts of active bismuth from HNO_3 solutions (288).

d. Alkylphosphoric Acid System

Methods were developed (189) for separating bismuth from a majority of accompanying elements such as Sn, Sb, As and Pb by extracting bismuth with alkyl phosphoric acids from H_2SO_4, HNO_3 and $HClO_4$ solutions. Bismuth is back extracted from the organic phase with solutions of HCl and HBr and their salts (82; 224).

e. High Molecular Weight Amine Systems

The distribution of Bi(III) and Po(IV) between HCl or HBr and xylene solutions of trilaurylamine has been studied by Sheppard and Warnock (289). The maximum extraction coefficient was ∿20 in 0.5-M HCl and ∿5.0 at 0.1-M HBr.

f. Miscellaneous Extractions

Bismuth-207 extraction from 0.5-M nitric acid with 0.1-M trioctylphosphine oxide (TOPO) in cyclohexane was reported (342). In this procedure, lead was irradiated with 21-MeV deuterons, and the target was dissolved in 8-M chloride-free nitric acid; the bismuth was extracted as described above with a yield of 90%.

Extraction of a mixture of Bi(III) and Hg(II) with tri-n-octylphosphine sulfide in 0.05-M cyclohexane has been reported (84). Quantitative recoveries were obtained from nitrate solutions. Bismuth is separated from large quantities of copper and iron by extraction from 0.5-2 N HCl solutions with 0.1-M n-octylamine sulfide in chloroform.

In the absence of chloride ions, the separation of bismuth from a number of other ions is achieved by extracting it with dibutylarsinic acid at pH 2.0 (247). The separation of bismuth from tellurium is made possible by extraction from 8-M HCl into iso-Pr_2O. Iron, As, Sb, Au, Tl, Sn, and Se accompany bismuth (144). These elements were determined photometrically.

2. Chelate Systems

a. Dithizone

Diphenylthiocarbazone or dithizone is a velvet-black solid which is somewhat soluble in most organic solvents. The solvents used most exclusively in the analytical applications of this reagent are CCl_4 or $CHCl_3$. Dithizone purification can be accomplished simply as described by Sandell (281).

The room temperature solubility of dithizone in chloroform is about 2 grams per 100 ml and in carbon tetrachloride about 0.05 gram per 100 ml. A dilute solution of dithizone in both of these solvents is green in color. Sandell (281) has written a comprehensive review on the role of dithizone.

Metal dithizonates are formed according to the reaction

$$M^{n+} + nH_2Dz \rightleftarrows M(HDz)_n + nH^+$$

Dithizonates of some metals, notably Cu(I), Cu(II), Ag, Au(I), Hg(II), Bi(III), and Pd change from the primary $M(HDz)_n$ to the secondary $MDz_{0.5n}$ form in basic solution: $2M(HDz)_n \rightleftarrows M_2Dz_n + nH_2Dz$.

Bismuth(III) is quantitatively extracted as a primary dithizonate by excess of dithizone solutions in CCl_4 (25-50 μM) in the pH range 3.0-10.0.

It is observed from reference 7 that bismuth can be extracted from a weakly acid medium, but lead requires a neutral or mildly alkaline solution for its extraction. Similarly, Ag, Hg, Cu, Po and Pd, etc. require dilute acid solution for their extraction as dithizonates; however, Zn, Cd, Co and Ni require either neutral or basic medium. Bismuth and a number of metals such as Pb and Zn are less easily extracted as the pH is increased in the alkaline range.

In order to obtain a higher selectivity in dithizone reactions which cannot be achieved by mere pH regulation, extensive use of masking agents such as cyanide, thiocyanate and thiosulphate has been made (281).

It is interesting to note that dithizone can be used to extract trace amounts of polonium from ammoniacal potassium cyanide or ammonium citrate solution (148), and it has been used to separate radiochemically pure RaE(^{210}Bi) from radiolead (^{210}Pb) RaD.

The cause of an inconsistency in the dithizone extraction of trace of bismuth from acidic solutions was clarified by Ashizawa, *et al* (12). They observed a minimum extraction of bismuth at pH 4 in the presence of citric acid and at pH 6 in the presence of halogen ions. This tendency was increased in the $CHCl_3$ solution more so than in CCl_4. Although the pH range 2.5 to 3.5 had been hitherto considered as an optimum condition for the extraction of bismuth, they recommended that the extraction be carried out at pH 1.5, adjusted by HNO_3 and NH_3 in the presence of acetate ions. Under these conditions even traces of bismuth could be separated completely from 1 g of lead. Phosphate and sulfate are observed to disturb the extraction. The optimum conditions given by them for the quantitative extraction of bismuth are 10 ml volume of dithizone solution in CCl_4 (10^{-3} M) per 50 ml of the aqueous phase of pH 1.5 (12).

For many radiochemical applications the separation of bismuth and lead is important. If macro amounts of either bismuth or lead are present, as in the case of cyclotron targets, a preliminary separation of the major constituent is necessary. This is done by either precipitation of lead as $PbSO_4$ or bismuth as oxychloride. Bismuth can then be separated by extracting it from a buffered solution at pH 2.6 to 3.0 with 0.01% dithizone in chloroform, as described by Rudenko (274). A similar separation has been made by dithizone in chloroform (18), and by Fisher and Leopaldi at pH 2.8-3.0 using dithizone in CCl_4 (93). Bouissieres and Ferradini have investigated the purification of ^{210}Pb (RaD), ^{210}Bi (RaE) and ^{210}Po (RaF) mixtures by extracting with dithizone (44).

The solubility of bismuth-dithizonate in carbon tetrachloride or in chloroform is rather low ($\sim 1.2 \times 10^{-5}$ M) (150). In the presence of cyanide, the extraction of bismuth becomes rather selective, for only Pb(I), Tl(I), and Sn(II) react with dithizone under these conditions.

Tin and thallium do not react in the stannic or thallic state, and lead can be separated from bismuth on the basis of the very different values of extraction constants of the dithizonates of bismuth and lead.

Solutions of bismuth dithizonate in CCl_4 absorb strongly at 490 nm (ϵ = 80,000 l $mole^{-1}$ cm^{-1}). This complex is destroyed by shaking with dilute ammonia; therefore, for the determination of bismuth only extractive titration or the mixed color method can be used. The dithizone method has been used for the determination of traces of bismuth in copper, in high-purity lead (after a preliminary extraction of bismuth as cupferrate), in high-purity tellurium (301), and in biological materials.

The separation of Pb-Bi-Po by extraction chromatography, using a dithizone-CCl_4 system and hydrophobized Celite 545 as the supporting material, is reported (286). That polonium is extracted by dithizone in CCl_4 or $CHCl_3$ from dilute mineral acid solution (148), (44) and that the extraction constants of lead and bismuth dithizonates are different [$\log K_{Pb(HDz)_2} = 0.44$, and $\log K_{Bi(HDz)_3} = 9.98$], have been used in determining conditions for their separations. In Figure 12 are given plots of log q vs log (HCl) for polonium and bismuth and actual separations of RaD-RaE and RaF are demonstrated in Figure 13.

b. Cupferron

Cupferron, ammonium salt of N-nitrosophenylhydroxylamine is a white crystalline compound melting at 163-164°C. It is soluble in water and in alcohol. Generally an aqueous solution (∿6%) of the reagent is used.

Furman, Mason and Pekola (106) made a systematic study of the extraction of various metals by this reagent. Quantitative extraction of bismuth by 0.005-M cupferron in $CHCl_3$ takes place in the pH range 2-12.

Sugihara (313) recovered ^{214}Bi (RaC) from water of hot springs by extraction with a 1% solution of cupferron in $CHCl_3$, with the pH of the aqueous phase adjusted to 1. Chalmers and Svehia (57) described a systematic procedure for the separation and determination of 27 elements from solutions which included bismuth. A 5% aqueous solution of cupferron was used as the complexing agent and $CHCl_3$ as the extracting solvent.

Elements extractable by cupferron at various pH values of the aqueous phase were listed by Gibson (109). Gibson showed that Bi can be separated from Zn, Cd, Hg, Mn, Co, Ni and Pb by extracting it from aqueous solutions at pH 1.0 with a 1% solution of cupferron in $CHCl_3$. Bode and Heinrich (40) made a systematic study of the separation of bismuth from lead using cupferron. In the presence of iron (20 mg) as a carrier, bismuth is quantitatively extracted with 1% cupferron solution in chloroform.

After separating lead-210 from biological material by dithizone extraction Zbigniew (350) separated the bismuth-210 daughter with cupferron. Low background beta-counting was used to measure the beta activity of the daughter ^{210}Bi.

Results obtained in the determination of bismuth (0.1 to 1%) in an aluminum alloy in the presence of Pb, Fe, and traces of As, Sb, and Cd are reported (72). Bismuth was spectrophotometrically determined as the iodide complex after its extraction at pH ∿1.0 from the aqueous phase containing tartaric acid and cupferron.

An apparatus for the continuous extraction and separation of Al, Bi, and Pb from Fe employing cupferron as the extracting agent is reported (322). A substoichiometric extraction method using cupferron in chloroform was developed (287) for the determination of bismuth in the presence of 50-60 fold concentration of antimony. Bismuth extraction was done at pH 4.5 from an ammonium citrate buffer.

c. Thenoyltrifluoroacetone (TTA)

Thenoyltrifluoroacetone (TTA) is a crystalline solid melting at 43°C. The trifluoromethyl group in the compound increases the acidity of the enol form so that extractions at very low pH are feasible. This reagent is generally used as a 0.1-0.5 M solution in benzene or toluene (224). Bismuth is quantitatively extracted (225) by 0.25-M HTTA in benzene at pH >2.5.

Extractions with TTA have been used for separation of many metal ions. It permits extraction from stronger acid solutions than other chelating agents. Problems due to the instability of some chelates such as DEDT-carbamates in mineral acids are also avoided in TTA extractions. The high power dependence of the extraction on acidity makes, in addition, the separation of one metal ion from another very sharp. Typical extraction curves for Bi and a number of other ions are shown in Figure 3. It is apparent from this figure that Bi can be effectively separated from Th, Po, Pb, Ac, Tl, and Ra by a careful control of pH of the aqueous solution.

Thallium (III) is extracted by TTA in the acidic range, whereas Tl(I) is extracted in the neutral region. The separation of thallium from Bi is, therefore, facilitated by addition of a reducing agent such as hydroxylamine hydrochloride to keep thallium in the univalent state. Bismuth is then extracted around pH 2, and Tl(I) remains in the aqueous phase.

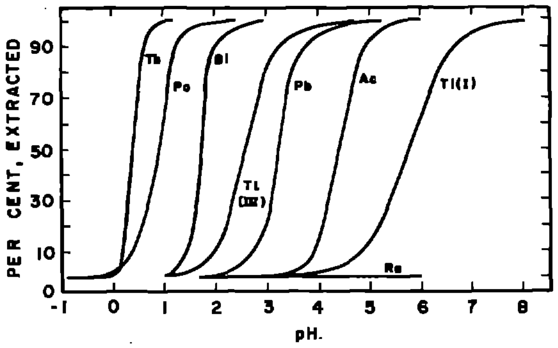


Fig. 3. Extraction of tracer quantities of thorium, polonium, bismuth, lead, thallium, radium and actinium from aqueous solution by an equal volume of 0.25-M thenoyltrifluoroacetone (TTA) in benzene (124). Reproduced by permission; see p. 128.

Poskanzer and Foreman (253) have reviewed the TTA extractions of various elements. The pH values corresponding to 50% extraction into 0.2-M TTA in benzene are given by them. Traces of bismuth are extracted quantitatively by a

0.25-M solution of TTA in benzene at pH of about 2.0. This method is selective for bismuth, although a few other metals are also extracted at this pH (124).

d. 8-Hydroxy Quinoline (8-Quinolinol or Oxine)

8-Quinolinol (8-hydroxy quinoline, oxine) is freely soluble in alcohol, chloroform, benzene, and aqueous solutions of mineral acids, but is almost insoluble in ether and water.

Oxine extraction has been studied in detail for a large number of metals. Quantitative extraction of bismuth occurs in 0.1-M oxine solution in chloroform, in the pH range 2.5-11.0 (224). Employing a more dilute solution of about 0.01 M, quantitative extraction of bismuth is achieved in the pH range 4.0-5.2.

Moeller (222) extracted bismuth oxinate into chloroform from a solution of pH above 4.0 and measured its optical absorption at 395 nm. The interference from copper, iron, nickel, and zinc was removed by complexing these elements with cyanide.

A systematic study of the solvent extraction of metal oxinates was undertaken by Stary (300). He studied bismuth oxinate extraction in the presence of various complexing agents such as oxalic acid and tartaric acid, and then calculated from this study the extraction constants of bismuth and other metal complexes and their stability constants with these water-soluble, complexing agents.

e. Sodium Diethyldithiocarbamate (Cupral)

Sodium diethyldithiocarbamate (Cupral, DEDTC) is a white crystalline compound readily soluble in water, but less so in alcohol. The reagent decomposes rapidly in acid solutions of low pH. Low pH extractions should, therefore, be carried out without delay and with an excess of the reagent to offset decomposition. Normally, a 1-2% aqueous solution of the reagent is employed.

Bismuth is quantitatively extracted as a yellow complex at pH 4-11 with CCl_4 containing 0.01-0.03 M NaDEDTC. The bismuth complex has its maximum absorption at 360-370 nm (ϵ_{max} = 8620 l $mole^{-1}$ cm^{-1}) (39). However, a measurement of the absorbance at 400 nm, although less sensitive, is specific for the Bi-complex (59).

The selectivity of the reagent can be improved by the use of masking agents such as EDTA, cyanide, citrate, tartrate, etc. At pH >11 in the presence of EDTA (∿0.006 M) or cyanide (∿0.03 M), the extraction of bismuth is very selective. Only thallium (III) is extracted under these conditions (39).

Separation of Bi from Pb and Cd can be achieved by selective extraction of bismuth employing $CHCl_3$ as a solvent. The remaining last traces of Pb and Cd, if any, can be removed from the organic phase by stripping with 0.2-M HCl (231). The reagent has also been used for the determination of bismuth in high purity gold and silver (301), in vanadium and niobium (231), and in various alloys (59).

A method of separating Bi and Pb is to extract them as carbamates from a citrate solution of pH 7 by a mixture of amyl alcohol and toluene in equal volumes. Lead is then stripped off the organic phase by treatment with 0.5-M HCl. Bismuth remains in the organic phase. Thallium accompanies bismuth under these conditions (39).

f. Diethylammonium-diethyldithiocarbamate

This reagent (DADTC or DDDC) in CCl_4 can be prepared as described by Bode and Neumann (41).

Bismuth can be quantitatively extracted within a wide pH range (from 10-N H_2SO_4 or 3-M HCl to pH 12) by a 0.4% solution of DADTC in CCl_4. The extraction of bismuth from 5-6 M HCl with a 1% solution of DADTC in chloroform is used for its separation from lead (307; 320).

A convenient method of separating lead from bismuth is to extract lead with the $CHCl_3$ solution of the reagent from 1.5-M HCl, leaving bismuth and thallium in the aqueous phase. Zinc, Cd, Sn(IV), In, and Pt(IV) extract with Pb to a greater or lesser extent, but Mn, V(V), Ce(III), U(VI), Sb(V), Cr(III), Zr, Ti, and Al remain with Bi and Tl. Bismuth is then extracted from 6-M HCl (41; 301). By extracting bismuth from 5-M H_2SO_4 it can be quantitatively separated from Pb and Zn.

Sill and Willis (292) used DADTC in chloroform to separate lead and bismuth from large quantities of other metals in strongly acidic solution. Dithizone was then employed to eliminate the remaining interference and to separate the two from each other. Separation of lead and bismuth from each other was better than 99.9%.

Conditions for separation of bismuth from various elements are reviewed in Table XI.

TABLE XI. SOLVENT EXTRACTION OF BISMUTH FROM VARIOUS SOLUTIONS BY DIETHYLDITHIOCARBAMATE (DEDTC) AND SIMILAR COMPOUNDS

Separated from	Solvent System	
	Aqueous Phase	Organic Phase
Copper	DEDTC and cyanide (241)	CCl_4
High purity Nb-Ta	Studied over a wide range of acidity (colorimetrically determined)	$CHCl_3$
	Tetramethylene DEDTC complex in EDTA, CN^- and ammonia solutions (buffering to pH ~9.5)	CCl_4 or $CHCl_3$ (The absorption measured at 420 nm)
Pb concentrates and Cu products	Double extraction in presence of EDTA, CN^- to complex copper	$CHCl_3$
Cd, Cu, Pb, Hg or Ag	Ammoniacal solution containing EDTA and CN^- (59)	CCl_4
Nb or Ta metal	Tartrate-cyanide solution, pH 11 to 12 (231)	$CHCl_3$
Cast iron	Extraction of Fe from HCl into isobutylacetate; Bi + Pb in ammoniacal tartrate and CN^-	$CHCl_3$
NaCl	A buffered solution of sodium chloride (157)	$CHCl_3$

g. 1-Pyrrolidinecarbodithioic Acid, -Ammonium Salt (APCD)

This reagent forms water-insoluble complexes with most metals except the alkali metals and alkaline-earth elements. These complexes can be extracted into ketonic solvents such as methyl isobutyl ketone or 2-heptanone. Malissa and Schoffmann (202) reported on the precipitation of various elements with APCD (and not APDC) at various pH values. They also studied its reactions in the presence of cyanide and tartrate as the masking agents. An extensive study of 1-pyrrolidinecarbodithioate as an extractant in the presence and absence of EDTA has been described (345). Considerable literature has developed on the use of APCD in atomic absorption determinations (265; 272; 296).

The bismuth complex of APCD in CCl_4 absorbs strongly at 360 nm and the molar extinction coefficient ε at this wavelength ε_{360}=9860 l mole^{-1} cm^{-1} (296).

In the atomic absorption determination of bismuth, the complex has been extracted into methyl isobutyl ketone. Because of its lower water solubility, 2-heptanone has also been used for extraction (202; 203). Bismuth has been determined in steel by APCD with EDTA and KCN as masking agents (174; 175). The reagent APCD has the main advantage that it can be used in acidic solutions. Procedures have been developed by Kalt and Boltz (155).

h. Dalzin, 1,6-Diallyl-2,5-Dithiobiurea, $(CH_2:CHCH_2NHCSNH)_2$

Dalzin has been studied in detail for the determination of various elements by Gupta and Sen Sarma (92) and by Dutt and co-workers (cited in 92).

A radiochemical method for the separation of bismuth activities such as ^{210}Bi, ^{212}Bi and ^{214}Bi in a wide variety of geological samples was developed by Rao *et al* (267). The procedure consisted of extracting bismuth from the sample solution at pH 2.0 with Dalzin in chloroform. Bismuth recovered from the organic phase by back extraction with 2-M acid was radiochemically pure. Advantages of this method over that employing dithizone are discussed in Ref. 267. A related reagent, 1-allyl-2,5-dithiobiurea, called "Monalzin" has the advantage of greater solubility than Dalzin in aqueous solutions (92).

Bismuth has been separated from uranium by precipitation or solvent extraction with 1-phenyl-1 H-tetrazole-5-thiol. Many of the elements occurring in bismuth-uranium alloys do not interfere. These include Pb, Zn, Fe, Mg, and Al. When uranium is present in large amounts, the bismuth must be extracted into a chloroform solution of the reagent. The solubility and stability of the metal chelates formed by bismuth and several other elements with 2-amino-1,3,4-thiadiazole-5-thiol have been reported (92). The use of masking agents improves selectivity (245).

Extraction of bismuth by other organic solvents is surveyed in Table XII.

H. Ion Exchange

The principal advantages of ion exchange as an analytical tool and its importance in radiochemical separations have been reviewed in detail by Kraus and Nelson (176).

This technique is versatile, inexpensive, readily available, and can be used to concentrate, separate, isolate, and identify radionuclides. The important

TABLE XII. A SURVEY OF THE EXTRACTION OF BISMUTH BY VARIOUS OTHER ORGANIC REAGENTS

Organic reagent	Extraction conditions
Acetylacetone (HAA)	Bismuth not extracted by 0.1-M HAA in benzene at any pH. (Be, Sc, Th, Fe, Cu, Tl, Ga, In, etc. are extracted quantitatively). Uranium has been quantitatively separated from as much as 5,000 times as much Bi in presence of EDTA and at a pH ∿6.0.
Benzoylacetone (HBA) (acetylbenzoylmethane)	Begins to extract at pH values higher than 7. Maximum extraction is obtained with 0.1-M HBA in benzene at pH 10-11.
Methyl oxime (MOx)	Forms a precipitate with HMOx which can be extracted into chloroform at pH ∿10.
Salicylaldoxime	A yellow complex is formed with the reagent which can be extracted into chloroform. After extracting Cu with 0.1-M solution of the reagent in iso-BuOAc at pH = 4.0, the heavy metals are extracted in 2:1 C_6H_6-iso-BuOAc by raising the pH of the aqueous phase to 9.0 with NH_3-NH_4Cl buffer.
N-Benzoyl-N-phenylhydroxylamine	Bismuth is precipitated with this reagent at pH ∿3.0. The precipitate can be extracted with chloroform.
8-Mercaptoquinoline (Thio-oxine) (HTOx)	In the pH range 3.5-11.0 a precipitate is formed by HTOx with bismuth which is quantitatively extracted into chloroform.
Di-(p-diphenyl) thiocarbazone	This has been used for the extraction of bismuth as well as other elements such as Ag, Cd, Cu, Hg, Pb and Zn.
Di-(p-chlorophenyl) thiocarbazone or (p,p-dichlorodithizone)	A 1.1 x 10^{-4} M solution of the reagent in CCl_4 has been used for the extraction of bismuth (log K = 11.25).
Di-(p-bromophenyl -thiocarbazone)or (p,p-dibromodithizone)	Extractable complex is formed with bismuth (log K = 11.1). It has a maximum absorbance at 500 nm.
Di-(p-iodophenyl-thiocarbazone) or (p,p-diiododithizone)	The reagent has been used for the extraction of micro amounts of bismuth. When using 1.1 x 10^{-4} M solution of the reagent in CCl_4, log K = 9.75. The bismuth complex absorbs at 505 nm.

TABLE XII. (Continued)

Di-(β-naphthyl) thiocarbazone	Using ~10^{-4} M solution of the reagent in CCl_4, bismuth (III) is extracted at pH ~2.0. Log K = 6.75. The complex absorbs at 520-530 nm with $\epsilon_{max} = 1.7 \times 10^5$ (48).
Diethyldithiophosphoric acid	Bismuth forms with this reagent a yellow complex which is extractable into an organic solvent.
2-mercaptobenzthiazole	Forms a precipitate with bismuth which can possibly be extracted into an organic solvent.
Tetraphenylphosphonium chloride	$(Ph_4P^+)(BiI_4)$ is quantitatively extracted into chloroform from 1-M sulfuric acid and measured at 505 nm. Antimony is masked with tartaric acid to prevent it from extracting with bismuth.
Tri-n-butyl phosphate (TBP)	Using perchloric acid (0.1-0.6 M) and thiourea, the bismuth complex is extracted with TBP. This complex is then measured absorptimetrically at 470 nm. From 2 M HNO_3-4 M HCl solution astatine can be extracted by 2% TBP in isopropyl ether keeping Bi, Po, and Pb in aqueous medium. Bismuth extractions from HNO_3 into DBP and TBP are useful for preparing high purity bismuth solutions. Bismuth extraction with TBP from 1-M HCl permits the group concentration of Cu, Ni, Co, Mn, Pb, Cr, Al, alkali metals, alkaline earths, rare earths and other elements in the analysis of bismuth.

advantage of the ion-exchange technique to radiochemical separations is that there is no lower limit to the concentrations at which it can be used, and that it is not necessary to add "carriers" as one might do in precipitation procedures (132; 142; 205; 280).

1. Cation Exchange

Mercury, lead, and bismuth are loaded on Dowex 50 in 0.1-M HCl and are separated by varying the concentration of the acid (109).

Kahn and Langhorst (152) have described an interesting method for the preparation of carrier-free ^{212}Pb (ThB) using Dowex 50. The procedure involves refluxing a thorium nitrate solution in 1-M HNO_3 in a Soxhlet extractor, in which the usual extraction thimble is replaced by a small (22 x 55 mm) cation-exchange column (Dowex 50 X 8, 100-200 mesh resin, in the hydrogen form). The thoron (^{220}Rn) which escapes from the boiling solution is carried along with the vapors into the upper part of the apparatus where the water vapor condenses.

Here, the thoron collects and decays by alpha emission to ^{216}Po which further decays to ^{212}Pb. The ^{212}Pb is washed onto and is retained by the resin and can be removed subsequently with 1-M HCl. Lead-212 (ThB) then decays to ^{212}Bi (ThC) by beta decay. Bismuth-212 can be separated from lead on anion exchange resin, employing dilute HCl (see pages 69,70) to elute lead.

Fritz and Karraker (102) have reported the use of ethylene diammonium perchlorate solution to effect group separations on Dowex 50 X 8 resin.

Radhakrishna (263) succeeded in separating ^{210}Bi (RaE) from ^{210}Po (RaF) by adsorbing the mixture on Dowex 50 (50-100 mesh) from 0.1-M to 0.3-M HCl. The bismuth activity was then eluted with 2-N HNO_3. Polonium was recovered by washing the resin with 2-N HCl.

Bismuth forms a strong anionic complex with HCl at all concentrations (0.1 M-12 M) (233). Hence, even in 0.5-M HCl bismuth is not adsorbed by cation exchange resin. This fact is used in the carrier-free preparation of ^{214}Bi (RaC) from ^{226}Ra by Glau *et al* (113). They first purified ^{226}Ra on anion exchange resin Nalcite-WBR using 2-N HCl and kept it aside for a month or so for the formation of all the daughter products before ^{210}Pb (RaD). The later decay products were not formed in high yield, because of the long half-life of RaD (19.4 years). Subsequently, this month-old radium preparation, relatively free from RaD, RaE and RaF etc., was adsorbed on cation-exchange resin Nalcite HCR in 0.5-N HCl. Bismuth-214 (RaC) passed through as anions, but radium and other decay products remained adsorbed on the resin. This method produced carrier-free RaC containing less than 1% RaB (Pb-214), and completely free from any radium.

Bismuth-212 has been separated in high purity from ^{212}Pb on a small Dowex 50 X 12 column with 0.5-M ammonium lactate solution. Bismuth is eluted by ammonium lactate solution due to the formation of a negatively charged complex; however, lead remains adsorbed under these conditions.

Separation of lead and bismuth is suggested (2) on the basis that the EDTA complex of bismuth is very stable in acid solution, while lead is not complexed. By percolating a solution containing lead and bismuth in EDTA at pH 1.8-2.5 through a cation-exchange column, the lead ions are completely adsorbed by the resin, and bismuth is eluted. Using ^{212}Pb-^{212}Bi, Abrao (2) obtained bismuth with a purity greater than 99%. The contamination was determined by gamma-ray spectrometry.

Anionic complexation with EDTA and citric acid has been used for the separations of Tl(I) from Bi(III) (266).

Thorium (^{232}Th, ^{228}Th) ions, after conversion to complex ions by the addition of reagents such as tartaric acid, citric acid, or EDTA, were not retained by a Dowex 50 cation exchange resin column in the sodium form. However, the decay products such as $^{224, 228}$Ra were retained. The amounts of recovery of the activities were of the following order: tartaric acid > citric acid > EDTA for the various reagents. Using 2-N HCl as the eluent, ^{212}Bi, ^{212}Pb and ^{228}Ra were removed from the column. Under these conditions ^{228}Ac was left behind and was eluted with 4-N HCl. For separation of ^{212}Bi from ^{212}Pb, anion exchange resin was used (233).

A fairly comprehensive list of equilibrium distribution coefficients of cations in HNO_3 and H_2SO_4 media in the concentration range 0.1 N to 4.0 N using Bio Rad AG 50W-X8 cation resin has been presented by Strelow *et al* (309) and their data are summarized in Tables XIII and XIV. If the distribution coefficients of Bi(III) in HNO_3 and H_2SO_4 are compared, it is evident that they are distinctly lower in HNO_3 than in H_2SO_4. This indicates that complex formation or association of these ions occurs in HNO_3. When compared to that in HCl, complexation occurs to a lesser degree in HNO_3 than in HCl. Sulfuric acid, because of its lower degree of dissociation, will supply a lower concentration of

TABLE XIII. VALUES OF K_d IN NITRIC ACID AND BIO RAD AG 50W-X8 CATION EXCHANGE RESIN (309)*

Cation	0.1N	0.2N	0.5N	1.0N	2.0N	3.0N	4.0N
Zr(IV)	10^4	10^4	10^4	6500	652	112	30.7
Th(IV)	10^4	10^4	10^4	1180	123	43.0	24.8
La(III)	10^4	10^4	1870	267	47.3	17.1	9.1
Hg(I)	10^4	7600	640	94	33.5	19.2	13.6
Fe(III)	10^4	4100	362	74	14.3	6.2	3.1
Pb(II)	10^4	1420	183	35.7	8.5	5.5	4.5
Bi(III)	$>10^4$	7430	371	61.0	8.0	3.7	3.0
U(VI)	659	262	69	24.4	10.7	7.4	6.6
Tl(I)	173	91	41	22.3	9.9	5.8	3.3
Hg(II)	4700	1090	121	16.9	5.9	3.9	2.8
Ti(IV)	1410	461	71	14.6	6.5	4.5	3.4

*Reproduced by permission; see p. 128. Data for Bi(III) corrected by private communication from F. W. E. Strelow, November, 1976.

hydrogen ions than either HNO_3 or HCl. Therefore, distribution coefficients in H_2SO_4 are distinctly higher than in either HCl or HNO_3. On the other hand a number of cations such as Zr(IV), U(VI), Ti(IV), etc. show marked complex formation or ion association in H_2SO_4. This leads to a substantial decrease in the respective distribution coefficients in H_2SO_4 compared to that of Bi(III), as shown in Table XIV. Bismuth separation from these cations is therefore feasible in H_2SO_4 medium.

TABLE XIV. VALUES OF K_d IN SULFURIC ACID AND BIO RAD
AG 50W-X8 CATION RESIN (309)*

Cation	0.1N	0.2N	0.5N	1.0N	2.0N	3.0N	4.0N
La(III)	10^4	10^4	1860	329	68	24.3	12.1
Bi(III)**	10^4	10^4	6800	235	32.3	11.3	6.4
Hg(II)	7900	1790	321	103	34.7	16.8	12.2
Fe(III)	10^4	2050	255	58	13.5	4.6	1.8
Th(IV)	10^4	3900	263	52	9.0	3.0	1.8
Tl(I)	452	236	97	49.7	20.6	11.6	8.7
Tl(III)	6500	1490	205	47.4	12.0	7.2	5.2
Fe(II)	1600	560	139	46.0	15.3	9.8	6.6
U(VI)	596	118	29.2	9.6	3.2	2.3	1.8
Ti(IV)	395	225	45.8	9.0	2.5	1.0	0.4
Zr(IV)	546	474	98	4.6	1.4	1.2	1.0
Al(III)	10^4	8300	540	126	27.9	10.6	4.7

*Reproduced by permission; see p. 128.
**Determined for q = 0.06 because of limited solubility.

Distribution coefficients of a number of cations on Dowex 50-X4 in 7-M HCl, 9-M HBr and 9-M $HClO_4$ are given in Ref. 234. In Fig. 4 are plotted values of the distribution coefficient against concentrations of HCl and $HClO_4$ for antimony, bismuth, and lead, Some typical cation-exchange separations involving bismuth are shown in Figs. 5-7.

Methods for separating bismuth from several elements are outlined in Tables XV and XVI.

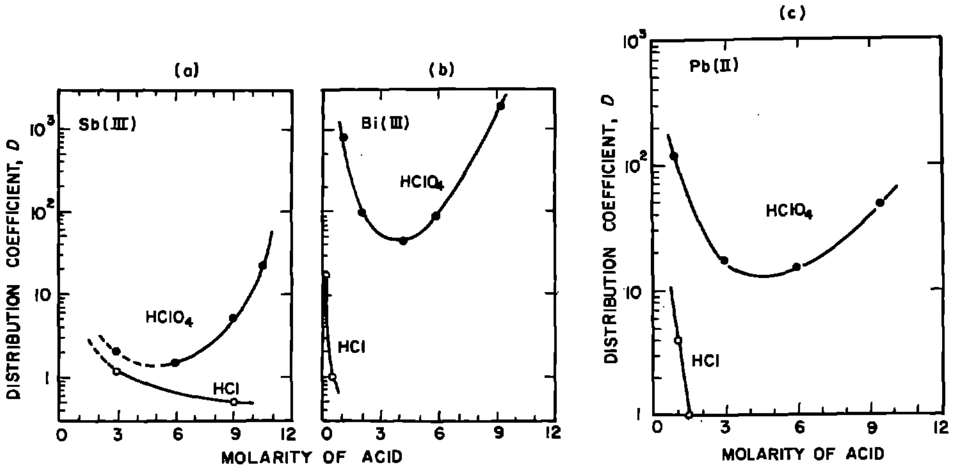


Fig. 4. Distribution coefficients of Sb(III), Bi(III), and Pb(II) on Dowex 50 cation-exchange resin in HCl and $HClO_4$ solutions (234). Reproduced by permission; see p. 128.

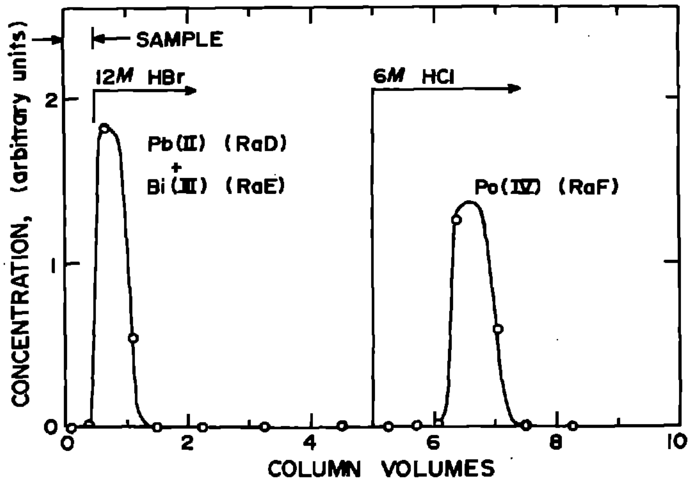


Fig. 5. Cation exchange separation of RaD, RaE, and RaF on a Dowex 50-X4 column, 0.28 cm^2 x 3 cm, at 60°C.

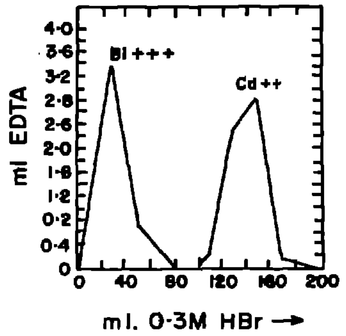


Fig. 6. Bismuth-cadmium separation on Dowex 50-X8 column with 0.3-M HBr.

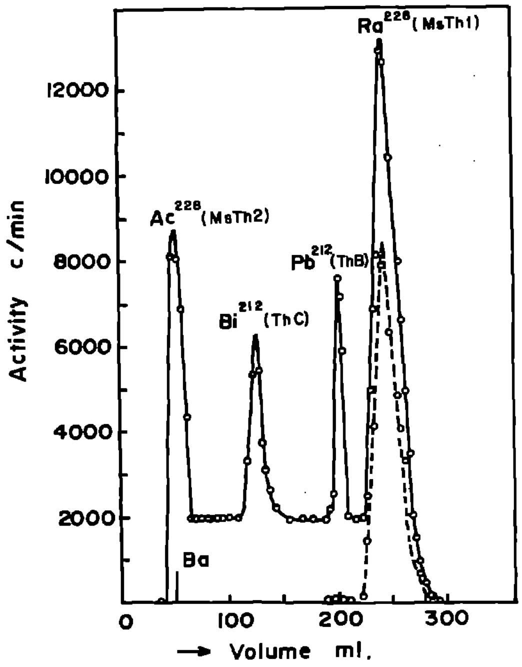


Fig. 7. Separation of ^{232}Th decay products on Dowex 50 using EDTA solution (81). Reproduced by permission; see p. 128.

TABLE XV. SEPARATION OF BISMUTH(III) FROM SEVERAL ELEMENTS BY CATION EXCHANGE RESIN WITH VARIOUS ELUENTS

Separated from	Resin Employed	Eluent and Other Details
Antimony	Dowex 50W-X8 (50-100 mesh)	Antimony eluted with 2-M $HClO_4$ + 0.2-M tartaric acid and Bi with 3-M HCl and water.
Copper	Dowex 50W-X8 (3 x 25 cm)	Bi eluted with 250 ml of 1-M HCl.
Iron (40 mg Fe/ml)	Dowex 50W-X8 (100-200 mesh)	Column washed with 20 ml of 1-M HF and elution done with 4-M HNO_3-1-M HF mixture..
Pb minerals	Dowex 50W-X8	Sorption in 0.3-0.5-M $HClO_4$; Bi elution with 100 ml of 0.008-M EDTA in 0.3-0.5-M $HClO_4$.
Lead	Dowex 50-X8 1.2 x 16 cm col.	Elution with 0.5-M HCl (Pb eluted from heated column with 0.6 M HBr)
	Amberlite (IR-120) (Na^+)	5% $NaNO_2$ for Pb and 2-M HCl for Bi.
Many elements including cadmium	Dowex 50-X8	Gradient elution with NH_4OAc, $NaNO_3$, H_2SO_4, HNO_3, NH_4Cl, HCl, etc. (1.5-M H_2SO_4 for Cd and Bi separation)
Pt group, Hg, Pb and Cu	KU-2(I) (2mm X 7-10 cm)	0.5-M HNO_3 for Pt metals; 0.01-M HCl + 0.4-M HNO_3 for Hg, 0.5-M HCl for Bi and Cd and 1.5-M HCl for Pb and Cu, in that order.
$Th(NO_3)_4 \cdot 4H_2O$	Dowex 50 (Na^+)	Thorium eluted with complexing agents: tartaric acid, citric acid or EDTA at lower pH (∿3.0). ^{212}Bi eluted with 2-M HCl.

TABLE XVI. ANION EXCHANGE SEPARATION OF BISMUTH(III) FROM VARIOUS ELEMENTS

Separated from	Type of Resin Used	Eluent and Other Details
Arsenic and Antimony	Dowex 21K (Flow rate 0.5 ml per min.)	Dilute HCl, HNO_3 and H_2SO_4 elute As. Antimony 2-M H_2SO_4; Bismuth, 1-M H_2SO_4 + 2-M $HClO_4$.
As, Pb, Fe, etc., in converter dusts	Various types, e.g., EDE-10P, AV-16, etc.	Sorption with H_2SO_4 + NaCl mixture and desorption with either H_2SO_4 or $H_2SO_4 + (NH_4)_2SO_4$.
Cadmium	Anion Exchange Resin	Cd, desorbed with 0.05-N HCl. Bi, eluted with 2-N H_2SO_4.
Cd, Cu, Pb, Ag, and Zn	Anion Exchange Resin, dia. 0.25-0.5 mm, ht. 10-13 mm, Flow rate 1-2 ml/min.	Zn eluted with 0.65-M HCl; Cd, 0.25-M HCl; Pb, with H_2O; Bi, 5-M H_2SO_4; and Ag, 3-M NH_4OH.
Silicates	Amberlite IRA-400 (8X, 100-200 mesh) 1 cm^2 x 20 cm	2-N HCl for sorption and washing, sequential elution of Fe, In, Zn, Cd, Sn, Tl and Bi with 0.25-N HNO_3.
Uranium (traces)	Quarternary amine-type anion exchanger	Sulfate solution at pH 1-1.5 retains uranium on the resin; bismuth passes through.
Metallic Sb	EDE-10P (anion exchanger)	Bismuth elution with 2-N H_2SO_4.

2. Anion Exchange

a. From Hydrochloric Acid

The adsorption of Bi(III) and Pb(II) on Dowex-1 resin, 200-300 mesh, has been investigated in detail by Nelson and Kraus (233). The adsorption of bismuth was very high in dilute HCl ($D > 10^5$ in 0.05-M HCl) and decreased slowly with increasing HCl concentration. This high adsorption of bismuth in dilute HCl is sufficient to permit its separation from most of the elements in the periodic table, except from a few such as Po(IV), Tl(III), Hg(II) and Au(III) etc. The adsorption of Pb(II) was low in dilute HCl ($D = 1$ in 0.05-M HCl). It is, therefore, easy to separate Bi(III) from Pb(II) on anion exchange resin employing either dilute HCl (≃0.05-M HCl) or concentrated HCl above 8<u>M</u>. Under these conditions Bi(III) is retained on the column and Pb(II) is eluted.

Ishimori (147) used Amberlite XE-98 to separate RaD, RaE and RaF from each other after adsorbing the mixture in HCl. ^{210}Pb(RaD) was eluted with 2-M HCl, ^{210}Bi(RaE) by concentrated HCl, and finally ^{210}Po(RaF) by HNO_3.

Chien and Haung (347) separated Pb and Bi from Ra using Amberlite IRA-400 resin. With 2-M HCl, ^{228}Ra passed through without retention, but ^{212}Pb and ^{212}Bi were adsorbed on the column. They eluted lead with 8-M HCl, which left bismuth on the column. Bismuth was finally removed by 2-N H_2SO_4.

Neutron-irradiated bismuth was separated from polonium (166) on Wofatit SbU or Amberlite XE-98 using concentrated HCl. In this acid polonium remains strongly adsorbed on the anion exchange column, while bismuth is eluted. Polonium is then desorbed with HNO_3 (1:1) or $HClO_4$ (1:1) from XE-98, or with concentrated $HClO_4$ from Wofatit SbU.

Adsorption behavior of about 40 elements was studied systematically in HCl on a weakly basic anion-exchange resin, Amberlite CG4B, by Kuroda *et al* (178). They showed that certain separations, such as lanthanides-thorium, Te(IV)-Bi(III), Sn(IV)-Sb(III), which are difficult to achieve on a strongly basic anion exchange resin in pure aqueous HCl solutions are possible on weakly-basic anion-exchange resin.

b. From Hydrochloric Acid - Hydrofluoric Acid Mixtures

In many anion exchange separation procedures, HCl-HF mixtures are useful eluents. Although the adsorption behavior of Bi is comparatively unaffected by the presence of HF, a number of elements such as Ge(IV), Sb(V), Sn(II), Ti(IV), Zr(IV) and Hf(IV) exhibit a different behavior in HCl-HF mixtures so that their separation from bismuth becomes simpler.

Trace amounts of Bi(III), Mo(VI), Nb(V), Sb(V), Sn(IV), Ta(V), Ti(IV), V(V), W(VI) and Zr(IV) were separated successfully from 10 g of iron using Dowex 1 x 8 in 1-M HF. These trace metals were held extremely strongly by the resin, whereas iron was not retained (70).

The separation coefficients for ^{210}Pb(RaD) and ^{210}Bi(RaE) were determined using the anion exchange resin AB-17 x 14 and HF solutions employing batchwise equilibrations, but the value of K_d for polonium-210(RaF) was determined from the activity peak of a chromatographic column filled with the same resin (235). A separation procedure for RaD, RaE and RaF was developed by these workers in which polonium was displaced from the anion exchange resin by nitric acid as an undissociated fluoropolonic acid.

c. From Other Electrolytes

Bismuth is strongly adsorbed from HNO_3 above 2-M concentration and is very strongly adsorbed from NH_4NO_3 solution. Under these conditions Pb is only weakly adsorbed; hence, separation of bismuth from lead is quite possible on anion exchange resin in a nitrate medium.

The elution behavior of various elements including bismuth on both cation exchange and anion exchange has been studied (201). Strelow and Bothma (308) studied the behavior of Bi(III) and other 51 elements on anion exchange resin (Bio Rad Ag1-X8, 100-200 mesh) in sulfuric acid media. The acid concentration range used was 0.01 N to 4.0 N.

d. Influence of EDTA

A complexing agent such as EDTA can drastically alter the adsorption behavior of an element on ion-exchange resins. The separation of ^{210}Pb and ^{210}Bi from HNO_3 on anion exchange resin in presence of EDTA can serve as an example (284). If a separation of these radioelements is attempted on a cation exchange resin with a non-complexing eluent, bismuth, because of its higher charge (+3), should be held more firmly by the exchanger than lead (charge +2). [With HCl as eluting agent, the fact that bismuth is removed from the cation exchanger much faster than lead in spite of its higher charge is due to the chloride complexing of bismuth, even in as dilute an acid as 0.5-M HCl.]

On the other hand, if the EDTA complexes of the two elements are formed at pH ∿4.7 the relative sizes of the charges of the two elements are reversed, and bismuth is present as a complex with a charge of -1 (BiY^-), and lead as a complex with a charge of -2, (PbY^{2-}). Lead is then held more firmly than bismuth by an anion-exchange resin. This property can be used to elute bismuth daughter activities from adsorbed lead isotopes.

e. Anion Exchange in Mixed Solvents

Korkisch and his collaborators (172) have described procedures for the separation of bismuth from various elements, using mixed solvents and anion exchange resins. In one such experiment they adsorbed the mixture of Bi, U and Th on the resin (Dowex 1 X8) in 96% n-propanol and 4% 5-M HNO_3. They eluted uranium with a mixture of 80% methanol and 20% 5-M HNO_3. The resin was then washed with a mixture of 80% methanol and 20% 6-N HCl to elute thorium. Finally, bismuth was removed by washing the column with 1-M HNO_3.

Methyl glycol and nitric acid are used to separate Bi from Pb, Cu and Fe, etc. (90). Korkisch and Feik (171) succeeded in separating Bi from Pb and lower lanthanides (La to Nd), by using tetrahydrofuran and nitric acid.

Ion exchange procedures for separations of Bi(III) from several elements with mixed solvents are summarized in Table XVII.

3. Chelating Resin

An investigation was made of the uptake of trace elements from both distilled water and sea water by the chelating ion exchange resins Chelex-100 and Permutit S 1005. Quantitative removal of Bi, Cd, Co, Cu, In, Ni, Pb, lanthanides, Si, Th, Y and Zn from resin was achieved by 2-N mineral acid.

A batch technique was used by Gorga and Lai (116) to evalute the ion-exchange properties of Chelex-100 for tracer elements from sea water. Blasius and Brozio (34) describe chelating ion exchange resins. A combination of solvent extraction and ion exchange resin separation was utilized for developing a rapid and quantitative method for the isolation of traces of metals from sea water (sodium matrices). Dithizone and TTA were used as extracting agents for most of the trace elements. Dowex 50 cation exchange resin was used to recover sodium (173).

TABLE XVII. ION EXCHANGE SEPARATION OF BISMUTH(III) FROM SEVERAL ELEMENTS USING MIXED SOLVENTS

Separated from	Type of Resin Used	Eluent and Other Details
Cu and several elements	Dowex 50 X 8	Formic acid + aq. dioxane
Cu(II), Cd, Zn, Fe(III), Hg(II), Mg, Co(II), Ni, Pb, Ca, etc.	Dowex 50 X 8	In 0.1-M trioctylphosphine oxide in tetrahydrofuran - 5% 12-M HNO_3, all these metal ions have high K_d values and hence can be separated from Bi.
Cobalt	Dowex 50 X 8	Co uptake with 80% acetone + 20% 3-N HCl. Elution with 90% acetone + 10% 6-N HCl.
Iron, Aluminum and Indium	Dowex 1 X 8	Bi and In separated by 0.6-M HBr in 20-40% alcohol. Bi from Fe and Al by 0.15-0.9-M HBr and 6-M HCl in 90% aliphatic alcohol.
Many elements	Dowex 1 X 8	Various alcohols and HNO_3; HNO_3 + acetone + tetrahydrofuran mixture.
Rare Earth elements	Anion exchanger	1.5-M HNO_3 in 85% isopropyl alcohol. Pb and Th remain with Bi on the column.

I. Chromatography

The term "chromatography" denotes a procedure in which a solution of the substances to be separated is passed, in a direction determined by the arrangement of the apparatus, over a more or less finely divided insoluble, organic or inorganic solid, resulting in retention of the individual components to different extents. The components are then separated by sequential elution with appropriate solvents (298; 131).

Spain (299) employed precipitation chromatography for the separation of bismuth and other sulfide group elements. He precipitated these elements as sulfides from 6-N HCl and achieved the separation on agar gel columns with 2-M sodium acetate and 0.1-M $(NH_4)_2S$.

Dithizonates of Bi, Cu, Cd, Pb, Ni, Zn, Co and Hg were separated on a column of potassium citrate or on potassium bicarbonate with CCl_4 as eluent (49).

From a 15 cm X 2.5 cm column of zeolite-225, Marti and Herrero (210) separated Bi from Ni, Cu, Co, Mn, Ca, Zn and Fe. Bismuth was eluted with 0.5-N HCl. Calcium, Ni, Cu and Fe were then eluted separately with 2-N HCl and Co, Mg, Mn and Zn individually with 4-N HCl.

1. Paper Chromatography

Paper chromatography is based on the use of adsorbent paper strips which furnish ready-made columns of a suitable medium. This separation method seems to be ideally suited for many radiochemical applications. But radiochemists have been slow in adopting the procedure to their separation problems, in spite of the fact that a number of excellent reviews are available on this topic (36; 125; 188).

Paper chromatography works best with trace amounts of material and does not involve any complex equipment. It is quantitative, convenient, and does not require much attendance when in progress. After the separation is achieved, radioactivity measurements can be made on sections cut from the paper, or in some cases the resultant activity can be removed from the strip by a suitable solvent, concentrated to a small volume, and evaporated on a planchet for counting.

Briefly, in this technique a drop of a solution containing a mixture of substances to be separated is placed on a filter-paper strip near one end and evaporated to dryness. This end is then placed in a suitable solvent mixture in a closed container. The solvent flows across the spot, called the origin, and along the filter paper strip. Ideally, each substance in the mixture moves along with the solvent at a unique rate, so that after a while all of the components of the mixture occupy distinct positions somewhere along the path of the solvent. The magnitude of this tendency of the movement depends on the details of the ion-solvent-filter paper interaction. This tendency is often different for different substances, so they become separated into bands along the filter paper. One has to select, therefore, a suitable filter paper, an appropriate solvent mixture, and a proper enclosure system for developing the chromatogram (36; 125) (see Fig. 8).

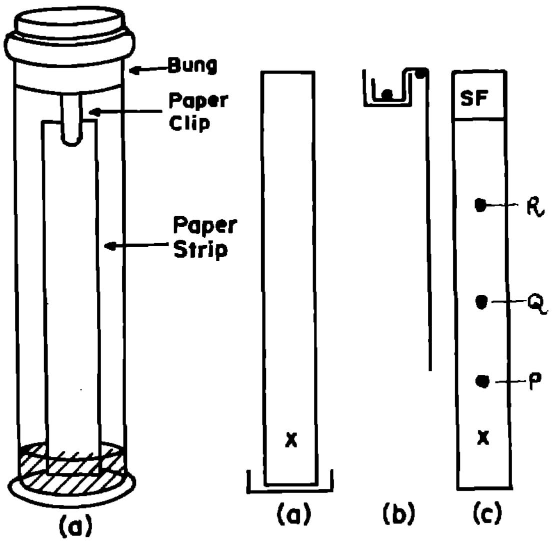


Fig. 8. Simple arrangements for separations by paper chromatography. (a) Ascending chromatography; (b) Descending chromatography; (c) A one-way separation, where X is the origin and SF is the solvent front. P, Q, and R are separated fractions (36). Reproduced by permission; see p. 128.

It is sometimes necessary to purify the filter paper before use, especially when working with traces of material. A number of methods used for purifying the paper have been described (241; 252).

A circular paper can also be used instead of the rectangular strip. In that case the sample mixture is to be applied at the center of the paper. A simple chamber can then be constructed from two evaporating dishes (36), as shown in Fig. 9.

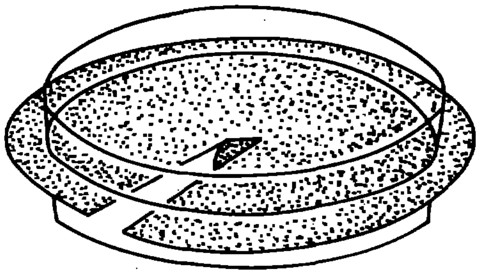


Fig. 9. A petri-dish arrangement for circular filter paper chromatography (36). Reproduced by permission; see p. 128.

When the separation is completed the paper is dried and the bands are located by radioactive measurements (98), or by colorimetric reactions as appropriate (188). The separated element can then be removed from the paper by cutting the required portion of the paper and digesting it, by leaching it with acid, or by treating it with a complexing agent such as EDTA solution.

The R_f value of a substance is defined as the ratio of the distance travelled by the substance to that travelled by the solvent front and is given as follows:

$$R_f = \frac{\text{distance from starting point to center of the band}}{\text{distance from starting point to the solvent front}}$$

The R_f values are relatively independent of the distance the solvent front has moved from the starting point or of the rate of solvent flow. In cases where the bands are abnormally wide, or where tailing of components occurs, larger differences in the R_f values are required. Otherwise, good separations can usually be achieved if the R_f values of the adjacent bands differ by 0.1 unit or more. In filter strip separations, it is normally sufficient to allow the liquid to flow up to about 20 cm or so.

Because of the restrictions on the quantity of the material to be handled (<200 μg) in paper chromatography it is often used as a final separation from complex mixtures after group separations have been performed.

In circular paper chromatography, the R_f values for similar conditions are generally larger than those for paper strip chromatography. These R_f values, which are sometimes referred to as R_{fc} due to the central feed system, are found to be closely equivalent to the square root of the R_f values obtained with rectangular paper strips.

2. Separations

A number of workers have used paper chromatography for the separation of ^{210}Pb(RaD), ^{210}Bi(RaE), and ^{210}Po(RaF) from a mixture. A two-solvent system was investigated for such a separation by Frierson and Jones (98). The first solvent mixture used was 50 parts butanol, 15 parts pyridine, 5 parts HCl, 10 parts acetic acid and 10 parts water. The second was made up of 60 parts butanol, 12 parts HCl and 1 part concentrated H_2SO_4. In both cases the presence of lead or bismuth carriers influenced the separation. The chromatograms obtained by them are shown schematically in Figs. 10 and 11.

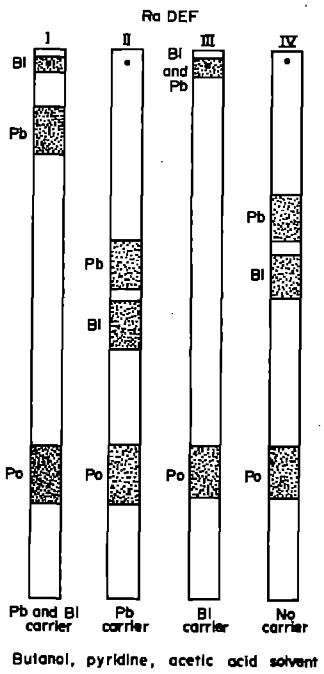


Fig. 10. Paper chromatographic separation of RaD, RaE, and RaF using butanol-pyridine-acetic acid solvent mixture (98). Reproduced by permission; see p. 128.

Using the ascending technique and butyl alcohol as a solvent, Glasoe (112) separated RaD, E and F from their mixture. The ^{210}Pb(RaD) was found principally near the bottom of the strip and the ^{210}Bi (RaE) near the top. Alpha counting revealed ^{210}Po (RaF) at the solvent front.

Many separations are indicated by the R_f tabulation by Gibson (109) and a few of the possible separations are discussed below.

Bismuth is well separated from all the elements listed in ref. 109 with butanol and 6-N HCl. On the other hand, butanol plus 1-N HCl separates bismuth from most of the elements except Cd(II) and As(III). A butanol-HNO_3 mixture is not very suitable for bismuth separations. Good separations of bismuth and

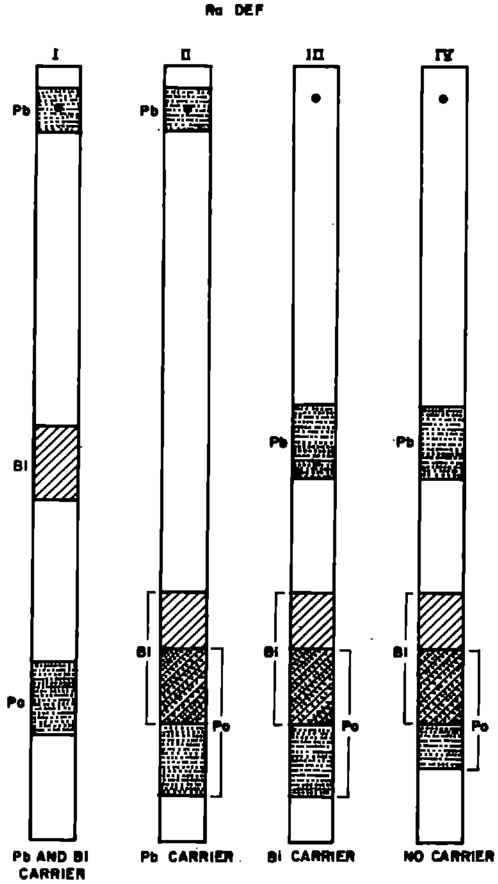


Fig. 11. Paper chromatograms showing RaD, RaE, and RaF separations with butanol-HCl-H_2SO_4 solvent mixture and the influence of the added carrier on the separation (98). Reproduced by permission; see p. 128.

lead are obtained with butanol-HBr mixture as a developing solvent, and in circular paper chromatography with butanol-HCNS.

Using commercial ethanol and HCl, good separations of bismuth from Pb(II), Hg(I), Ag(I), As(III), Cu(II), and Fe(III) can be achieved (187), whereas NH_4OH has been used to separate bismuth from Cu(II), Cd(II) and Hg(I); Pb(II) remains with Bi(III).

It is possible to separate Bi from Pb, Cu, Ag, As(III), Sn(II), Au(III), Hg(II), and Fe(III) by employing a mixture of isopropanol, butanol, and HCl

(327). Isopropanol with HNO_3 has been used to separate Bi(III) from Pb(II), Cu(II), Cd(II) and Tl(I) on paper. Lead and Bi were separated by using 0.4-N H_2SO_4. Lead remained at the starting point, and bismuth moved close to the solvent front. A novel "Gradient Elution" technique was developed by Lederer (187) for the separation of Bi, Hg, Cd, Fe, Ni, Cu, and Co.

Reeves (268) formed complexes of Ag, Al, Ni, Co, Cu, Bi, Zn, Cd, Hg, and Fe with 8-hydroxy quinoline and submitted the resulting mixture to chromatography. Anderson and Lederer (10) employed the descending technique and separated Cu from Bi, Ag, Au, Pt, Rh, and Hg using as solvent 1-butanol saturated with 2-N NH_4OH and dimethylglyoxime.

Improved separations are often possible if after the first development with one solvent, the paper is dried and developed with a second solvent in the same direction. Pollard, cited in ref. 125 resolved a mixture containing Al, Bi and Fe by this technique. Iron has a high R_f value in butanol-benzoyl-acetone solvent, but Al and Bi remain together at the starting point. If the paper is then dried and developed with dioxane-antipyrine solvent, bismuth moves and is separated from aluminum. The R_f values after movement are iron, 0.95; bismuth, 0.6; and aluminum, 0.06. See Tables XVIII and XIX.

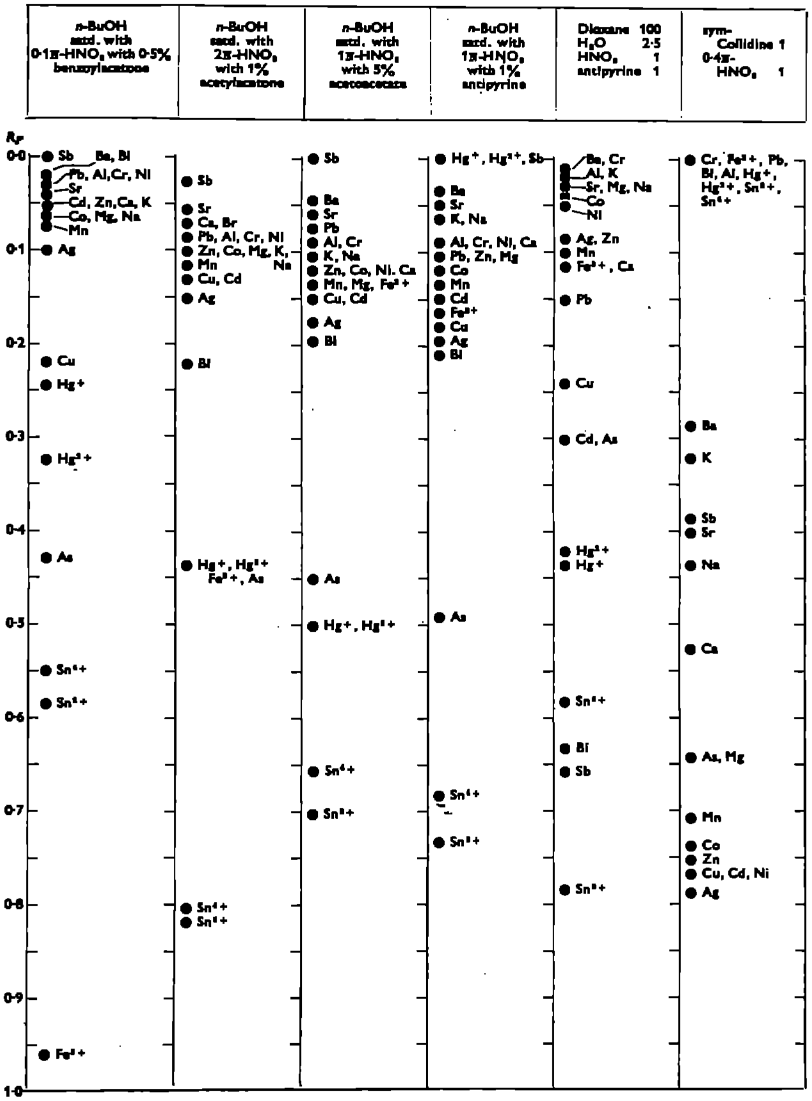
In the preparation of a sample, the cation mixture should be made up of chlorides or nitrates, since salts of these anions are usually soluble and show little tendency to hydrolyze (36). To prepare an unknown mixture for chromatography a 2% solution of it is made so that the final pH should be around 1.0 or so.

Feigl's monograph (89) gives a list of host of reagents for spot tests for bismuth. Various other color reagents used for bismuth and other inorganic ions are tabulated by Carleson (53) .

A 0.5% solution of rubeanic acid in 96% ethanol is a good general detection reagent. This reagent is suitable for most of the heavy metals. Very rich colors and a high sensitivity are obtained by exposing the sprayed chromatogram to ammonia (125).

Werner (125) investigated about 283 organic reagents for use in paper chromatography of inorganic ions. He found tetrahydroxyquinone to be the most universal and sensitive reagent. It was possible to detect about 26 cations, including bismuth, with this reagent.

TABLE XVIII. VALUES OF R_F FOR SOME CATIONS IN SOLVENT SYSTEMS WITH COMPLEX-FORMING AGENTS*



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*Reprinted with permission from I. M. Hais and K. Macek (eds.), "Paper Chromatography - A Comprehensive Treatise," p. 747, 1963. Copyright by Academia, Publishing House of the Czechoslovak Academy of Sciences.

TABLE XIX. PAPER CHROMATOGRAPHY OF BISMUTH, CADMIUM COPPER, LEAD AND MERCURY(II) (213)

Solvent	Salts	R_f in ascending order of value	Paper[a]	Method[b]
EtOH-5-M HCl (9:1)	----	Pb, Cu, Bi, Cd(front)	W 2	A
n-BuOH satd. with 1-M HCl	Cl	Pb(0), Cu, Cd, Bi, Hg(II)	------	A
n-BuOH satd. with 3-M HCl	Cl^-	Pb(0.0), Cu(0.27), Bi(0.60), Cd(0.77), Hg(II)(0.81)	------	A
	----	------------------	------	A
	----	Ag(0.0), Cu(0.20), Pb(0.28), Sb(III)-(0.39), Bi(0.7.), As(III) (0.82), Cd(0.83), Sn(II)-(0.86), Hg(II)(0.90)	B 202	A
n-BuOH-acetoacetic ester-aq. HOAc (75:1:15), pH 3.5-4	----	Pb, Cd, Cu, Hg(II)	W 3 or 4	A
t-BuOH-Me_2CO-H_2O-6-M HNO_3-acetylacetone (4:4:1.1:0.45:0.45)	----	Pb, Cd, Cu, Bi, Hg(II)	W 1	C
i-PrOH-HOAc-H_2O	----	Pb(0.24), Cd(0.34) Cu(0.44), Bi(0.51), Hg(II)(0.69)	W 1	C
BuOH-HOAc-12-M HCl-H_2O (4.5:1:0.1:4.4)	----	Pb(0.05), Cu(0.13), Cd(0.20), Bi(0.40), Hg(II)(0.78)	------	A

[a] Paper: W = Whatman; B = Benzer.

[b] Method: A = ascending; C = circular.

3. Reversed Phase Extraction Chromatography or Partition Chromatography

In partition chromatography, a liquid phase on a suitable support is used instead of a solid adsorbent as in adsorption chromatography. The solvent, or mobile phase, passes over the so-called stationary phase carrying the substances to be separated with it. The latter are partitioned between the two phases. The Nernst equation for the distribution of a compound between two immiscible phases applies. Here, the partition coefficient is a measure of the migration rate just as the adsorption coefficient is in adsorption chromatography. Since in this technique the stationary phase is non-polar and the mobile phase is polar, this is referred to as "reversed phase" partition chromatography (55).

Stronski *et al.*, (311) describe the separations of $^{212}Pb/^{212}Bi$ and $^{228}Ra/^{228}Ac$ by extraction chromatography. They use bis-(ethylhexyl) phosphate, adsorbed on powdered polytrifluoromonochloroethylene, as the extracting agent and hydrochloric acid at various concentrations as the eluent. The gamma-ray spectra of different fractions taken on a Ge(Li) detector revealed the success of the separation.

Sebesta (286) employed hydrophobized Celite-545 as the supporting material for 5 x 10^{-4} M solution of dithizone in CCl_4. He reported separations of Zn-Cd, Ag-Hg, Cd-Ag and Pb-Bi-Po by this extraction chromatography. The actual separation of RaD(^{210}Pb), RaE(^{210}Bi), and RaF(^{210}Po) as achieved by Sebesta using various concentrations of dilute HCl (0.1-1.5 N) is shown in Fig. 12.

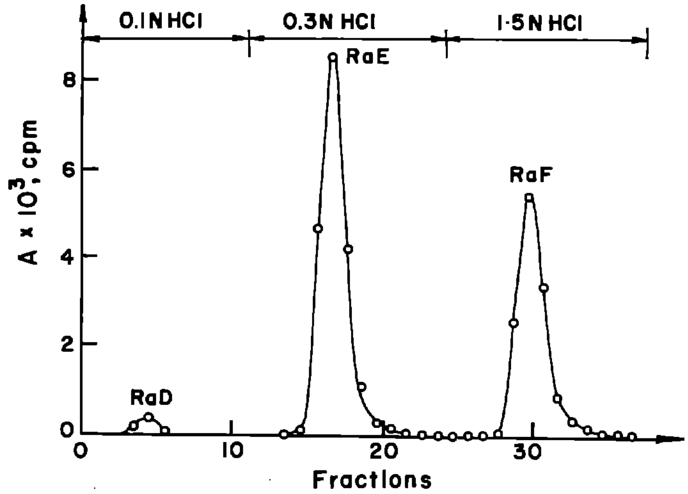


Fig. 12. Separation of RaD(^{210}Pb)-RaE(^{210}Bi)-RaF(^{210}Po) by partition chromatography, employing various concentrations of HCl (286). Reproduced by permission; see p. 128.

The flow rate in this separation was maintained at 0.5 ml cm^{-2} min^{-1}, and for ascertaining the separation, five drop fractions of the eluent were collected for analysis. He carried out the separation at 25-28°C. Figure 13 shows the dependence of log q on log [HCl] for polonium and bismuth.

Fritz and others (101) reported separation of iron from bismuth and many other elements by reversed phase extraction chromatography from 6- to 8- M HCl into 2-octanone, and also of tin from bismuth and various other ions on a solid support impregnated with isobutyl methyl ketone with 8-M HCl as eluent (103).

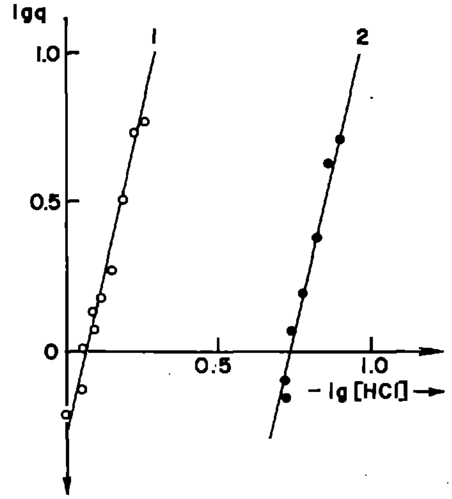


Fig. 13. Plots of log q *vs* - log [HCl] for Po (line 1) and Bi (line 2). Reproduced by permission; see p. 128.

A rapid method for the separation of bismuth from nickel and its concentration on fluoroplast 4 using diisoamyl phosphate as a stationary phase was reported (153). Detection of bismuth was achieved photometrically at 450 nm using xylenol orange at pH 1.45.

Tri-N-octylphosphine oxide has also been used as an immobile liquid phase on powdered polytetrafluoroethylene as a support. Lead and bismuth separation has been reported with 0.1-N and 10-N HNO_3 as mobile phases. The method was extended to the preparation of carrier-free ^{90}Y and ^{206}Bi. Kalyamin (156) describes a rapid method using Teflon and tributyl phosphate for the separation of Bi, Hg, and Ag from products formed in the bombardment of bismuth by high-energy particles. Samples were taken in 0.5-N HCl and passed through the column. Bismuth, Hg, Au, Tl, Re, Te, W and Ag were sorbed quantitatively; the column was rinsed with 0.5-N HCl. Bismuth and Ag were eluted from the column by rinsing it with 3 volumes of 5-N HCl, and then Hg was eluted with 8 column volumes of 11-N HCl.

A separation of bismuth and thallium was made (310) on a column (90 mm) packed with 150-250 mesh Teflon containing 0.4 g of adsorbed tributyl phosphate (TBP). Bismuth elution was done with 10-N acid, and thallium was eluted with 1-N NaOH. Brief descriptions of several procedures using reversed-phase, thin layer chromatography for bismuth and other ions are collected in Table XX.

TABLE XX. REVERSED-PHASE, THIN-LAYER CHROMATOGRAPHY OF BISMUTH(III) AND VARIOUS OTHER IONS

Elements	Layer (Stationary phase)	Solvent System (Mobile phase)	References
Ag, Bi, Cd, Cu, and Mn	Free amine cellulose impregnated with thiocyanate form of Amberlite LA-2	0.1-7 M NH_4SCN	118
Many elements	Cellulose impregnated with tributyl phosphate (TBP) and with TBP and TOPO	Various concentrations of aq. HCl and sulfates	20
A number of metal ions, including Bi	Silica gel-cellulose (5:2) impregnated with polysulfide polymers (Bi, Cu, Ag, Hg ppt. and remain at the starting point)	Methyl alcohol, ethyl alcohol, dioxane-HNO_3 media	236
Bi and other radioactivities from Au and Tl	Teflon impregnated with diethyl ether (80 mm x 2-3 mm)	2 N HCl eluted Bi & other activities; Au with 0.5 N HCl & Tl by 0.2 N HNO_3	254
Bi-Au(III) -Cd-U(VI)	Cellulose impregnated with Amberlite LA-2	HCl-NH_4SCN	179
Bismuth and other ions	Silica gel impregnated i) with bis(2-ethylhexyl) phosphate ii)with tri-n-octylamine and Amberlite LA-1	HCl, HNO_3, and KSCN hydroxy acids and glycerine; complexones at various pH	228

J. Electrochemical Techniques

In the preparation of radioactive sources, the uniformity and thickness of the deposit are of extreme importance. A thin, uniform source is essential to reduce problems associated with "back-scattering" and "self-absorption" in radiochemical or nuclear spectroscopic studies. As such sources can be obtained by electrodeposition, the technique is considered as one of the best known methods of preparation of radioactive samples. In addition, the improved sensitivity, selectivity, accuracy, and ease of automation of modern apparatus make electrochemical techniques the prime choice in many analytical problems. Several detailed discussions about these techniques are available elsewhere (19; 38; 69; 74; 78; 110).

1. Electrolytic Methods

These involve processes in which the separation of one or more constituents is effected by the passage of current through a solution under investigation. The two important techniques in this category are internal electrolysis and electrodeposition with applied potential.

a. Internal Electrolysis

This method has limited application, but for the determination of traces of more noble metals in the presence of much larger amounts of others, it is very satisfactory and easy to perform (190).

Recently, spontaneous electrodeposition of ^{207}Bi, ^{115m}Cd, ^{59}Fe, ^{114m}In, ^{125}Sb, ^{119}Sn and ^{204}Tl from 0.04 ml of catholyte on thin metallized plastic films has been reported (24). A magnesium ribbon was used as the anode.

Internal electrolysis has been applied to the determination of bismuth (0.001-0.3%) in lead. Bismuth is plated from a nitric-tartaric acid solution containing urea. A platinum gauze cathode and lead anode are employed. A similar method of determining bismuth in lead from a dilute solution containing $KMnO_4$ and hydrazine is reported (8). The electrolysis was carried out at 85°C for 15 minutes.

b. Electrodeposition

The determination of metals by electrodeposition is discussed in several reference works, e.g., ref. 78. The conditions which lead to a uniform, adherent deposit depend on the hydrogen over-voltage and other factors which influence the deposition of a metal from solution (190).

Hydrochloric acid solutions are normally employed in the dissolution of alloys and similar complex materials, with occasional additions of chlorate during dissolution. These solutions are, therefore, frequently used as plating baths. Evolution of chlorine from the anode must be avoided, since this causes attack of the anode, resulting in the codeposition of the anode material with the metal under investigation. This chlorine evolution is prevented by the use of suitable anodic depolarizers; hydrazine or hydroxylamine are most suitable for this purpose.

Sulfuric acid solutions are not used very often as plating baths. Nitric acid solutions are satisfactory for many analyses, and in such solutions, since the acid acts as a cathodic depolarizer, hydrogen evolution is inhibited. Thus, bismuth and copper are often deposited in poor form when hydrogen is liberated at the same time, but from HNO_3 solutions smooth quantitative deposits are obtained.

c. Bismuth Plating

Apparatus developed for the preparation of thin, uniform films of radioactive materials has been reported (140), and although usually developed for a particular purpose, such apparatus may be suitable for a wide range of applications. Parker (242) describes the plating of radioactive material employing a high-voltage power supply (∿600 V dc), and he calls it "molecular plating" because of the similarity of the form of the plated material to that originally present in the plating solution.

Bismuth can be deposited on platinum electrodes from a number of different electrolytes. Some of the established procedures are summarized in Table XXI.

Coche (64) has pointed out the critical effect of the nature and state of the electrode surface when depositing bismuth on platinum from solutions of 10^{-10} M to 10^{-13} M, i.e., for which the bismuth deposit is less than a mono-atomic layer.

An interesting procedure has been described which involves electrodeposition and dissolution of bismuth and copper together in a chromatographic column. From HCl containing 10^{-9} M bismuth and 10^{-9} M copper, Hahns and Helmut (127) co-deposited these elements on platinum at a current of 10^{-8} A for 50 minutes. They then placed the electrode on a cation exchange column of Dowex-50, and using the electrode as an anode they re-dissolved bismuth and copper with 10-N HCl, which was also used as the eluent. This chromatographic separation gave them two distinct peaks corresponding to bismuth and copper.

d. Bismuth Separation from Various Metals by Electrodeposition

Lingane (191) separated bismuth from other metals having reduction potentials differing by less than 0.2 V using a stirred mercury-pool cathode at -0.35 V *vs* SCE. The separation of bismuth and its determination in mixtures of Cu, Pb, and Sn; and of Sb, Cd, Cu and Ag by ingenious choice of electrolytes and potentials is also described by Lingane and Jones (192) and by Tanaka (317).

TABLE XXI. ELECTRODEPOSITION OF BISMUTH FROM VARIOUS PLATING BATHS

Bath composition	Potential	Electrode	Temp. °C	Time min	Reference
Nitric acid and hydrazine sulfate	-0.02 to -0.1 V	--	80-85	25	190
2.5 ml HNO_3+12 g sodium tartrate	--	--	100	20	
10 ml HCl + 5 g oxalic acid + 0.5 g hydraz. chloride	-0.15 V	--	80-85	20	
20 ml H_2SO_4 + 1 g hydraz. sulfate	-0.05 to -0.15 V and 1.2 A	--	10	20-30	
HNO_3 + hydrazine sulfate and sodium lauryl sulfate (Bi-207 deposn.)	3 V at 30 to 40 mA (vigorous stirring)	--	70	--	261
$BiCl_3$ in HCl and Trilon B complexing agent	Current density 2.7 A dm^{-2}	Pt (cathode) Cu (anode)	25	--	211
$BiCl_3$ in HCl and glycerol 30 ml/l	Current density 1.5-2.0 A cm^{-2}	--	--	--	13
Ammonium diethyl-amine-triamine-penta acetate in presence of $NaHSO_4$ + HF	(99.9% deposition of Bi-207)	--	25	50	260
Tartaric-succinic acid-NH_3 buffer (initial pH 7.2-8.5) in presence of $N_2H_2 \cdot 2HCl$	-0.20 V *vs* SCE	Cu plated Pt	--	--	4

Harrison *et al.* (128) devised an interesting method based on controlled potential electrolysis. They separated ^{212}Bi (ThC) from other radiochemical decay products (ThB, ThC' etc.) by direct deposition onto metal disc cathodes fitted for use with "planchet" counters.

Codeposition of bismuth and antimony from perchlorate-fluoride solutions containing 0.1-M bismuth and 0.41-M antimony was studied using a copper cathode and a platinum anode system. Effects of temperature, concentration of the electrolyte, and current efficiency were studied. Deposits obtained were compact, dull, and adhered strongly to copper (167).

2. Potentiometric Titrations

A novel potentiometric method for bismuth and various other metals, based on the use of a mercury indicator electrode, was developed by Reilley and Schmid (269). At the start of the titration of bismuth with EDTA, a drop of a dilute solution of Hg-EDTA is added. The following equilibrium is established: $Bi^{3+} + Hg\text{-}EDTA \rightleftharpoons Bi\text{-}EDTA + Hg^{2+}$. This equilibrium lies far to the right, and remains there during most of the titration as bismuth is complexed by EDTA. At the stoichiometric point, the low concentration of mercury(II) is complexed by EDTA, and the potential drops sharply. As in the case of amperometry, selectivity in these potentiometric titrations can be achieved by the use of masking agents or by pH control.

In another bismuth titration by potentiometry, excess of EDTA is added to a bismuth solution and the excess is back-titrated with ferric solution. The presence or absence of EDTA affects the redox potential of the ferric-ferrous couple. The only difficulty in this titration is the somewhat slow rate of reaction of ferric iron with EDTA.

A mixture of Bi, Cd and Ca was analyzed by potentiometric titration of Bi at pH 1.2. The Cd titration was done at pH 4.0 and that of Ca at pH 8.0.

Hannema and co-workers (126) developed conditions for obtaining sharp end points in compleximetric back-titrations of mixtures of metals such as Bi, Cu, Ni and Zn potentiometrically, with EDTA as the ligand and Th(IV) as the titrant.

3. Amperometry

A general discussion of amperometry as related to trace analysis is given in the reviews by Maienthal and Taylor (198; 199). The most important member of a class of complexing agents of great analytical importance is EDTA. A solution of the disodium salt is used as the actual titrant, and the anion is usually written as H_2Y^{2-}.

EDTA forms 1-to-1 chelates with nearly all di-, ter-, and quadri-valent metal ions, M^{n+} as follows:

$$M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)+} + 2H^+.$$

This equation shows that an increase in acidity displaces the equilibrium to the left, so that metal ions may then escape appreciable complexation unless their EDTA chelates have high stability constants. For example, if the pH is kept between 1 and 2, bismuth can be selectively titrated in the presence of many other metallic ions (258). This pH adjustment increases the selectivity of an otherwise very unselective titrant. Another approach involves the addition of a moderately selective substance that can form complexes of even greater stability than those formed by EDTA. Copper and zinc interference, for example, can be prevented by addition of cyanide, which strongly complexes or masks these ions (97).

Recently, a scheme of amperometric titration and polarization curves for various phases of titration by EDTA was developed by Vydra, Vorlicek, and Stulik (326) for Al, Ba, Bi, Cu, etc.

Goldstein *et al.* (114) have used iron(II) as an indicator ion in amperometric titrations with EDTA. At a potential of +0.4 V, iron(II)-EDTA chelate, but not iron(II) itself, is oxidized at a platinum electrode, so the current rises after the end point is reached. Sharp end points are obtained in the titration at pH 4.5 of most of the numerous metal ions that form EDTA chelates of stability constant K greater than 10^{18} (see Table XXII). These workers (114) have also used vanadyl sulfate solution as a back-titrant for EDTA, which permits the indirect determination of various metal ions. This is possible as the stability constant of the vanadyl-EDTA chelate is sufficiently low (log K = 18.8). The titration is carried out at the optimum pH of 4 ± 0.5 with a potential of +0.6 V applied to a platinum foil electrode of area 1 cm^2. Interference is caused by agents that oxidize vanadyl ion or are oxidized at a potential of +0.6 V (304). Bismuth is one of the ions that may be successfully determined by both the iron(II) indicator (324), and the vanadyl ion back titration technique of Goldstein, Manning and Zittel (114).

As stated earlier, bismuth forms a very stable complex with EDTA; therefore, it can be titrated with this reagent even when the pH is very low. Since the bismuth ion undergoes reduction at a dropping mercury electrode at a potential of less than 0.2 V, its determination in strongly acid mixtures of metal ions is subject to only limited chemical and electrical interference.

Pribil and Matyska (257) titrated bismuth at a dropping mercury electrode at pH between 1 and 2, using a potential of -0.16 to -0.20 V *vs* SCE and obtained an "L-type" titration curve. No interference is caused by the presence of Zn, Cd, Al, Pb, As, Cr, Mn, and Co. Sodium tartrate or citrate is required if Sb(III), Fe(III), or Ni(II) is present. Not more than a 5-fold excess of iron or nickel, or a 10-fold excess of silver or copper can be tolerated. A small amount of gelatin is necessary if bismuth is to be titrated in the presence of

TABLE XXII. STABILITY CONSTANTS OF SOME METAL-EDTA COMPLEXES*

Metal ion	Log K	Metal ion	Log K	Metal ion	Log K
Ag^{+}	7.32	Gd^{3+}	17.37	Ra^{2+}	7.07
Al^{3+}	16.13	Hg^{2+}	21.80	Sb^{3+}	24.80
Am^{3+}	18.16	Ho^{3+}	18.74	Sc^{3+}	23.1
Ba^{2+}	7.76	In^{3+}	24.95	Sm^{3+}	17.14
Bi^{3+}	26.47	La^{3+}	15.50	Sr^{2+}	8.63
Ca^{2+}	10.59	Li^{+}	2.79	Tb^{3+}	17.93
Cd^{2+}	16.46	Lu^{3+}	19.83	Th^{4+}	23.2
Ce^{3+}	15.98	Mg^{2+}	8.69	Ti^{3+}	17.7
Cf^{3+}	19.09	Mn^{2+}	14.04	Tl^{3+}	22.5
Cm^{3+}	18.45	Mo^{5+}	25	Tm^{3+}	19.32
Co^{2+}	16.31	Na^{+}	1.66	U^{4+}	17.50
Co^{3+}	36	Nd^{3+}	16.61	V^{2+}	12.70
Cr^{3+}	20	Ni^{2+}	18.62	V^{3+}	25.9
Cu^{2+}	18.80	Pb^{2+}	18.04	VO^{2+}	18.77
Dy^{3+}	18.30	Pd^{2+}	18.5	V^{5+}	18.05
Er^{3+}	18.85	Pm^{3+}	16.75	Yt^{3+}	18.09
Eu^{3+}	17.35	Pr^{3+}	16.40	Yb^{3+}	19.51
Fe^{2+}	14.33	Pu^{3+}	18.12	Zn^{2+}	16.50
Fe^{3+}	25.13	Pu^{4+}	17.66	Zr^{4+}	29.9
Ga^{3+}	20.27	Pu^{6+}	16.39		

*Ref. 290.

copper or silver ions. Since Sn(IV) is readily reduced and also forms an EDTA chelate that is reasonably stable at pH 1, this ion interferes under all conditions (304).

Bismuth can be determined by precipitation as bismuth oxyiodide, dissolution of the precipitate in dilute HCl, and amperometric titration of iodide ion at a stationary platinum electrode with $AgNO_3$ solution. No external emf source is needed, since the reference electrode is also of platinum and is immersed in a saturated mercury(I) nitrate solution. The potential of this reference system is about +0.6 V *vs* SCE. The titration can be carried out in the presence of Pb, Cu and Cd ions.

Another method for the amperometric titration of bismuth with iodide in the presence of certain organic compounds such as 8-quinolinol is reported (351). Aluminum, Co, Cr, Mn, Ni, Zn, NO_3 and SO_4 do not interfere. If chloride concentration does not exceed 0.1 M it, too, does not interfere. Cadmium and Cu must be absent.

The influence of the applied potential, pH, and stirring on the accuracy and selectivity in the determination of bismuth *via* EDTA titration with biamperometric end point indication has been studied by Vydra and Vorlicek (325). Al, Ba, Be, Co, Mg, Mn, Ag, Sr, Tl(I), U(VI), fluoride, perchlorate and sulfate in any concentration did not interfere with the bismuth determination. However, Fe(III) and Cu(II) in high concentrations, and Zr, Tl(III), and In even in small amounts, interfered.

Bismuth in a solution of pH 2 made from alloys containing lead has been titrated amperometrically with EDTA without the removal of Pb, which was precipitated as $PbSO_4$ by setting the potential at 0.9 V (321).

4. Polarographic Analysis

The concentration range which may be covered by conventional polarography (214) is, in general, from 10 to 0.01 mM, and the accuracy is of the order of several per cent. If the separation of the reduction potentials of different species is great enough, *i.e.*, 200 mV, several elements may be determined concurrently in the same solution.

Barker and Gardner (21) developed first "Square-Wave" and then "Pulse" Polarography. This development has permitted determinations at the 10^{-7}-10^{-8} M level, resolution of neighboring peaks of only 40 mV separation, and toleration of a 40,000-fold excess of prereduced ions.

Pulse techniques are probably of more use to the analytical chemist than square-wave techniques, because of their greater sensitivity for irreversible as well as reversible reductions, and their tolerance of low concentrations of supporting electrolytes. In square-wave polarography, supporting electrolyte concentrations of about 0.2 M must be maintained, which may add to blank difficulties in some trace-level determinations.

Bismuth Analysis by Polarography

An indirect method was developed by Pohl (251) for the determination of total Al, Pb, Fe, Ga, In, Co, V, Bi, Zn, and Zr in reactor water. He claims the procedure to be sensitive to several parts per billion of impurities, such as bismuth, with a variation of 5-10%. Utilizing pulse polarography, a similar procedure for the analysis of pure water is also described (43).

Polarographic studies of bismuth oxinate (-quinolinate, 8-hydroxy-) in methyl isobutyl ketone are reported by Dagnall and Hasanuddin (68). Bismuth has been determined polarographically, after its extraction with diethyldithio-carbamate in chloroform and in the presence of EDTA (146).

In the determination of lead and bismuth in lead ores, rocks, and cyanide solutions, a preliminary separation of these elements by ion exchange was carried out. Both these elements were adsorbed from 1-M HCl on anion exchange resin, and Pb was desorbed from the resin with dilute HCl. Bismuth was then eluted with 10% thiourea solution and determined polarographically in the citrate medium (314).

Methods employing both polarography and amperometry are reported for the determination of Bi, Cd, Co, Cu, Pb, Mn, Ni, Mo, V, U, Zn and sulfate and fluoride in ores, rocks, alloys, and other concentrates (135). Trace bismuth determination in tungsten and tungstates has also been achieved by this technique (315).

The dc polarographic behavior of As, Sb and Bi ions was studied at 80-130° in strong phosphoric acid medium at a dropping mercury electrode (117). After removal of the cadmium matrix, the trace impurities of Bi, Cu, Fe, Pb, Ni and Ag in the residue were determined spectrographically as well as polarographically (264). As a supporting electrolyte for bismuth analysis a mixture of 0.5-M H_2SO_4 + 1-M $MnSO_4$ + 0.1-M HCl + (8×10^{-4})-M methylene blue was employed.

Lagrou and Verbeck (180) reported the determination of traces of bismuth in cobalt by pulse polarography after their electrolytic separation. Bismuth separation from 50 ml of $CoCl_2$ solution in 1-M HCl was done in 4 hours at a cathode potential of -0.2 V on the mercury pool. An inverse polarographic method was also developed (66) to determine parts per billion concentration of bismuth.

A procedure based on anodic stripping polarography is described for direct determination of 10^{-5} -10^{-2}% bismuth and copper in lead. Electrolysis on a hanging mercury drop electrode was done at 0.25 V *vs* SCE in HNO_3 medium. Bismuth stripping was achieved in 1-M HCl and 1-M ethylenediamine at 0.4 V *vs* SCE (295).

A method was developed (312) for the simultaneous reduction of both bismuth and lead into the Hg pool and their detection by stepwise anodic stripping. Tartaric acid (0.4 M) in $HClO_4$ (0.3-0.72 M) was used as a supporting electrolyte.

K. Neutron Activation

Neutron activation analysis has been thoroughly described in various monographs (76; 138; 177) and in various review articles (94; 196; 206).

Bismuth has a low absorption cross section for thermal neutrons, about 0.0391 barn. Because of this low cross section, bismuth has attracted attention as a fuel carrier and coolant for nuclear reactors and as neutron windows in medical reactors. This low cross section has also made feasible the determination of trace impurities such as Ag, As, Sb, Cd, Cu, Mn and Na, etc. in metallic bismuth by neutron absorption (163).

The element bismuth is monoisotopic, with ^{209}Bi present in one hundred percent abundance. Thus, with the advent of nuclear reactors and their intense neutron fluxes, the reaction

$${}^{209}_{83}\text{Bi}\ (n,\gamma)\ {}^{210}_{83}\text{Bi} \xrightarrow[5d]{\beta^-} \underset{(\text{RaF})}{{}^{210}_{84}\text{Po}} \xrightarrow[138d]{\alpha} {}^{206}_{82}\text{Pb}\ (\text{Stable}).$$

has become economically feasible. A flux of 10^{14} n cm^{-2} sec^{-1} will produce 72.8 Ci/kg of bismuth in an irradiation period of 142 days (half saturation).

The ^{209}Bi absorption cross section for thermal neutrons is about 0.039 barn. The cross section for ^{210}Bi production in the above reaction in a thermal reactor is 0.020 barn, with the difference going to produce the long-lived ^{210m}Bi, which decays by alpha emission to ^{206}Tl. Hence, the determination of the beta activity of the product of neutron absorption by ^{209}Bi accounts for only about half of the neutrons absorbed.

Alpha counting is very rarely employed in activation analysis, because the very short range of alpha particles requires extreme care in preparing the sample in a form suitable for counting. Nevertheless, the high resolution of surface-barrier and diffused-junction semiconductor detectors allows very specific measurements. The very high detection efficiency and the inherently low background provide a high specific activity. De Boeck *et al.* (73) preferred the use of the alpha emitting ^{210}Po daughter over that of the pure beta-emitter ^{210}Bi for the determination of bismuth in lead irradiated by neutrons. Solvent extraction was used to separate ^{210}Po from interfering activities and the isotope was then deposited on a silver disc by spontaneous deposition of ^{210}Po. Despite the low activation cross section of the ^{209}Bi for the production of ^{210}Bi, less than 100 ppb amounts could be easily determined in one gram of the sample. The standard deviation was about 5% and was mainly governed by counting statistics. The alpha counting of the ^{210}Po daughter of bismuth is also considered a highly selective method for the neutron activation determination of bismuth in samples of complex composition (195).

Since the maximum permissible body burden for ingested polonium is only 0.02 μCi (4.5 x 10^{-12} g of ^{210}Po), safety precautions must be rigorously observed in the bismuth purification from ^{210}Po (91).

Neutron activation of bismuth and several other elements and its application to forensic studies have been described by Guinn (122). In the determination of bismuth in lead samples by neutron activation analysis it must be remembered that naturally occuring ^{210}Bi (RaE) can interfere. As a result of the occurrence of uranium in lead ores, this nuclide is present in variable concentration in recently fabricated lead. Through the manufacturing process, the series is interrupted at ^{210}Pb, so that the ^{210}Bi activity decays with the half-life of ^{210}Pb, namely,21 years. An experiment designed to estimate such an error has been described by De Boeck *et al.* (73).

1. Neutron Activation for Determining Trace Impurities in Bismuth

The presence of micro-amounts of certain impurities in bismuth metal enhances its characteristics as a semiconductor. On the other hand, certain trace elements such as Ag, Au, Cd, etc., which have relatively high neutron-capture cross section decrease the usefulness of bismuth as a reactor coolant. These trace impurities have been determined in bismuth metal by neutron activation analysis (6; 52; 343).

2. Neutron Activation of Bismuth Impurity in Various Samples

The data obtained by various workers on the determination of bismuth in a number of sources such as rocks, ores, pure metals, and related materials are presented in Table XXIII.

TABLE XXIII. DETERMINATION OF BISMUTH IN VARIOUS MATRICES BY NEUTRON ACTIVATION

Matrix	Experimental Details
Lead	Dissolution of the matrix in HNO_3, addition of carrier solutions, and isotopic dilution procedure (33).
	Destructive separation following neutron activation. Internal electrolysis (239).
Stony Meteorites	High resolution gamma spectrometry; chemical separation and beta-counting also employed (54).
Chondrites	Bismuth content of 143, 71 and 37 atoms per 10^9Si atoms determined in carbonaceous chondrites (60).
Meteorites and Standard Rocks	30 chondrites, 6 achondrites, and 8 separated meteoritic phases analysed (282).
	12 chondrites analysed (158).
Achondrites and Ocean Ridge basalt	18 achondrites and 4 terrestrial basalts analysed (184).
Lunar rock	Seven samples analysed (184).
Rocks and Ores	Flux: 1.8×10^{13} n cm^{-2} sec^{-1} for 2 to 8 hours. Cooling time: 8 to 12 days Alphas counted on ZnS(Ag) scintillator Sensitivity: 0.005% (194).
Ore Deposits	Flux: 10^{12} n cm^{-2} sec^{-1} Sensitivity: 10^{-7} to 10^{-6} g/g (349).
Silicates	Flux: 6×10^{13} n cm^{-2} sec^{-1} for 3 days Sensitivity: 1 ppb. Anion exchange separation employed. Low-level beta counting and semiconductor gamma spectrometry applied (206).
Micro-Ingots of Alloys	Non destructive analysis. Ge(Li) detectors used (181).
Minerals	Non destructive neutron activation (14).
Alloy steel and Residues from Electro-Etching of Other Steels	In addition to bismuth, 15 other elements were also determined (121).
Mo, W, and Graphite	Destructive separation and gamma-ray spectrometry (249).

L. Atomic Absorption Spectrometry

The basic principles of atomic absorption have been adequately covered in the literature (e.g., 7; 85; 270). An excellent review by Kahn (151) is available for those who are newcomers in this field.

Atomic absorption spectrometry, because of its high sensitivity, has been applied in the majority of cases for the determination of major, minor, or trace elements. In the case of a microtrace element, *i.e.*, an element with concentration below the normal detection limit, it becomes necessary to concentrate and isolate that element. The most popular technique, then, as applied to atomic absorption spectrometry is the extraction of the element or elements from an aqueous solution into an organic solvent. The most suitable organic solvents for use with atomic absorption have been found to be esters and ketones. The use of APCD as a complexing agent extracted into methyl isobutyl ketone (MIBK) as a means of concentration of an element is described previously.

For the determination of bismuth the 223.1-nm spectral line is most sensitive; up to 0.5 ppm bismuth can be detetermined. The next bismuth line of importance is at 222.8 nm and is about half as sensitive as the first one (273). The Bi 306.8-nm line is several times less sensitive and lies in the region of the strong absorption bands of hydroxyl radicals (250). According to Gatehouse and Willis (107), the sensitivity can be improved using low temperature flames. The fuel-to-oxidant ratio has no pronounced effect on the absorption of bismuth. Willis (340) used this resonance line at 306.8 nm for the determination of bismuth in urine. The interference from OH radicals was reduced by spraying the ketone solution directly into the flame. It also does not cause any unsteadiness in the absorption reading when sprayed into the flame.

Allan (5), too, considers 306.72 nm as the most sensitive spectral line for bismuth, employing a hollow-cathode current of 8 mA. The sensitivity was found to be 2.0 μg Bi/ml and the limit of detection was approximately 1 μg/ml. No interference was found from Ag(I), As(III), Cd(II), Cu(II), Hg(II), Ni(II), Pb(II), Sb(II), Sn(IV), Zn(II), or from Cl^-, PO_4^{3-} and SO_4^{2-}, up to concentrations of 50 times that of Bi(III).

Trace bismuth (100 ppb) in reactor sodium samples was determined by atomic absorption in the residue after vacuum distillation of sodium at 320°C.

It was observed that 100 ppm of tellurium enhanced the absorption due to bismuth, nickel, and chromium in the atomic absorption determination of these elements in 1-M HCl.

The sensitivity obtained for determination of bismuth in steels is 0.0005% Bi in low-alloy steels. This sensitivity decreases with increasing concentration of alloying elments such as nickel and chromium (197). Sattur (283) also determined bismuth in non-ferrous alloys.

In an oxyacetylene flame Marshall and Schrenk (207) did not find any interference with determination of bismuth in the presence of Ag, As, Cd, Cu, Hg, Ni, Pb, Sb, Sn, or Zn.

M. Vacuum Evaporation

The technique of vacuum evaporation has been adequately described by Ivanov *et al.* (149) and Kobisk (165). Condas (65) discussed the techniques and problems related to the production of thin films of bismuth.

In order to determine the desorption probability for ^{210}Bi(RaE) on nickel and gold surfaces, an apparatus was constructed (77) which allows active and inactive materials to be evaporated, and also to take the activity measurements as a function of time at several temperatures in high vacuum.

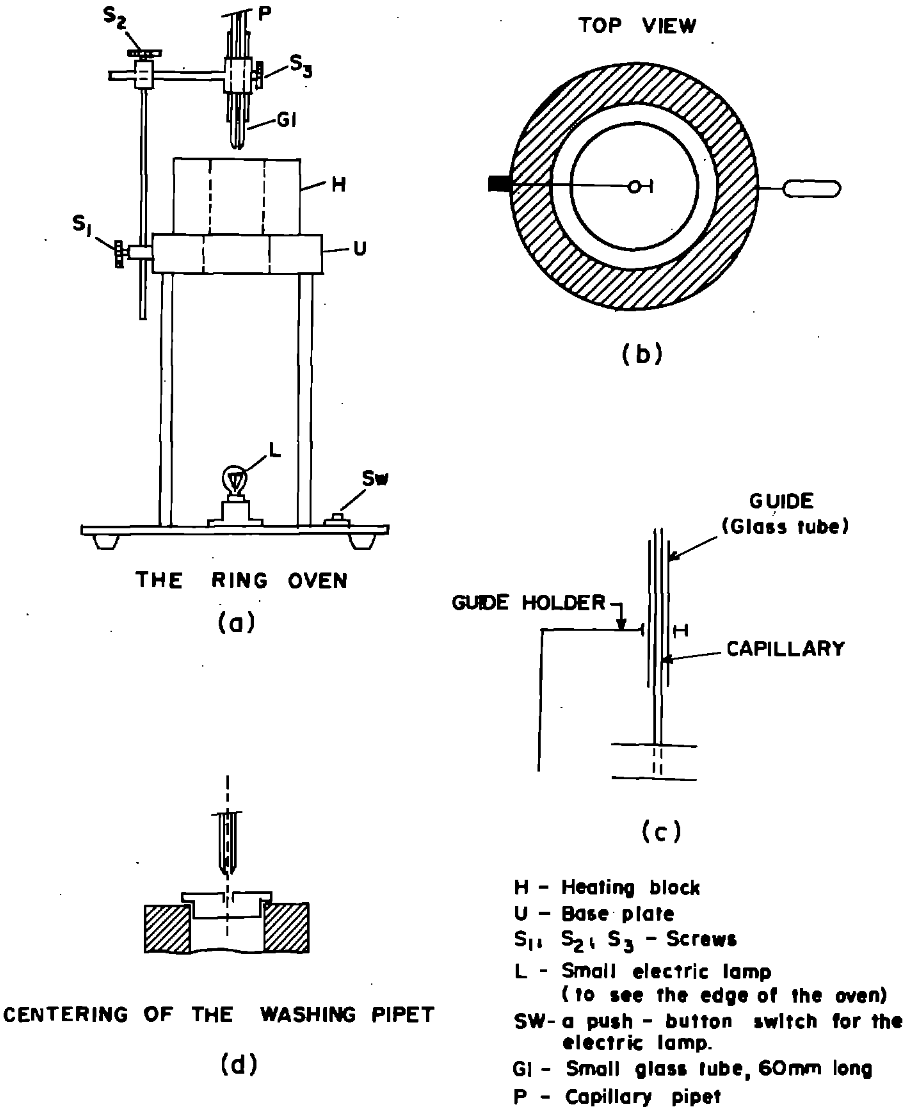
A United Kingdom Atomic Energy Report (11) describes separation of bismuth from niobium by volatilization of bismuth as the bromide, followed by ether extraction of niobium from thiocyanic acid in 4-M·HCl and 0.5-M tartaric acid media.

Most of the work reported in the literature on vacuum evaporation discusses separation of polonium (usually RaF) from bismuth (RaE). In air, polonium begins to sublime at 700°C and is completely vaporized at 900°C, while scarcely any bismuth sublimes below 1100°C. It is also found that mixtures of polonium and bismuth sulfides can be separated by vacuum sublimation (15). A large-scale separation of ^{210}Po from bismuth metal by molecular distillation is also described (60).

N. The Ring-Oven Technique

The ring-oven method originally developed by Weisz in 1954 can be employed for the separation of ions in one drop. The ring oven consists essentially (Fig. 14) of a cylindrical heating block of aluminum, provided with a central perforation of 22 mm inner diameter; other material such as stainless steel, copper, glass, etc. can be used instead of aluminum. A heating wire is installed in this block. An adjustable resistance serves to regulate the temperature of the heating block, which should be about 110-115°C at the surface.

One or more test drops are placed in the middle of a round quantitative filter paper (∿55 mm diameter) by means of a capillary pipette (331). One of the groups of the material is precipitated on the paper by means of



THE RING OVEN

(a)

(b)

(c)

CENTERING OF THE WASHING PIPET

(d)

Fig. 14. Apparatus used for the ring-oven technique, showing details of various accessories (332). Reproduced by permission; see p. 128.

an appropriate reagent (*e.g.*, H_2S, NH_4OH, etc.) and thus fixed in the fleck of the paper. The filter paper is then placed on the ring oven in such a manner that the fleck is precisely within the center of the hole in the heating block, just underneath the guiding glass tube (Gl, Fig. 14). The excess constituents of the sample which did not precipitate are then washed away by means of a suitable solvent (acid, NH_4OH, alcohol, water, etc.), applied by a capillary pipette which just fits into the narrow glass guiding tube, Gl.

Because of the capillary action of the paper, the material that has gone into solution in the wash liquid migrates outward and forms a concentric front until it reaches the edge of the opening of the heating block. There the solvent evaporates and the solutes are deposited in a very narrow, sharply outlined ring zone of 22 mm diameter.

Washing out procedures are controlled readily by the electrical lamp L, below the heating block. The zone between the initial spot and the "ring" is naturally free of sample components; consequently, the inner spot bearing the precipitated group of the sample can be cut out mechanically by means of a punch of a proper size. The precipitate on the little disc of filter paper can then be subjected to a proper preliminary treatment, such as oxidation, and then separated further by another precipitation. The little disc is then placed centrally on a fresh round filter and again extracted with an appropriate solvent on the ring oven, just as though the disc were nothing but an ordinary spot on the paper.

The resulting rings are about 0.1 to 0.3 mm in diameter. In other words, their surfaces are smaller than that of the initial fleck and consequently the concentration of the materials which have been washed out is actually higher in the rings than in the original fleck.

The filter paper is cut into several sectors, and on the individual sectors the various members of the corresponding groups are identified by spraying with suitable reagent solutions. Sharply outlined circular arcs of the respective color appear on the sectors if the substances in question are present.

With the aid of this method, a separation procedure has been worked out which includes (331; 332) fourteen ionic species, and which can be accomplished with a single drop (1.5 μl), which may contain as little as a few micrograms of a solid test material. An outline of the separation scheme is given in Fig. 15. The identification of the 14 metal ions is done by various spot-test reagents (332). A lead chloride-alkaline stannite test was employed (89) for the identification of bismuth. Various other spot tests for bismuth are given elsewhere (78).

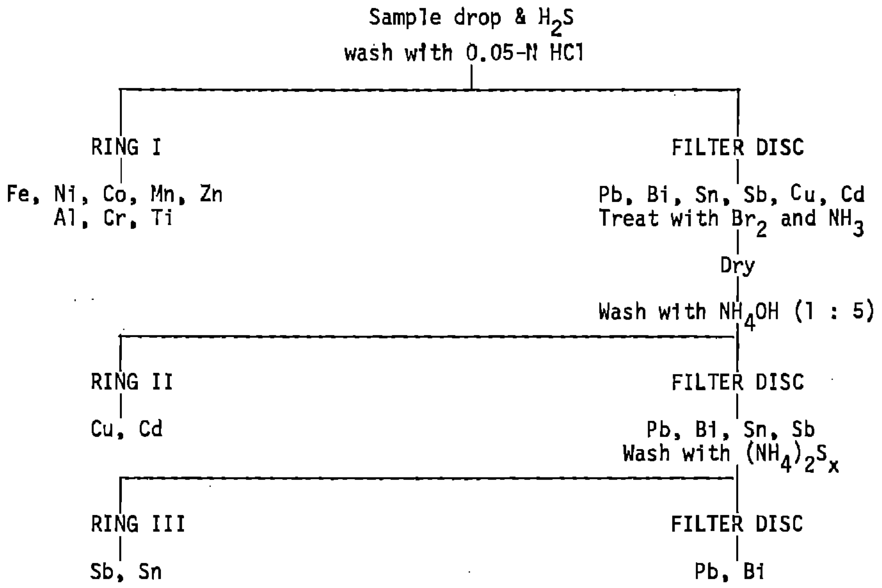


Fig. 15. Separation Scheme for 14 Metal Ions by the Ring Oven Technique.

Separation and identification of micro quantities of metallic ions such as Bi, Cu, Cd, As, Sb, Hg, Ag, and Sn by the ring oven with EDTA as the complexing agent has been described (294). Some additional accessories for use with the ring oven have also been proposed (336).

A glass ring oven has been described by Ballczo (17), who maintained the surface temperature of 105-110°C using *sym*-tetrachloroethylene (bp 121°C) as a bath liquid, which was heated with a conventional gas or electrical heater. Lately, the same author used a platinum lining for the surface and the inner cylinder of the hollow glass body, which has the advantage of improved heat conductivity.

Hashmi *et al.* (129) used an all-glass, nichrome-wire ring chamber for the separation and identification of 46 metal ions from a single drop of a test solution. Before actual analysis by the ring-oven technique, they separated the cations into six groups by liquid-liquid extraction.

The ring-oven method has proved to be very useful and versatile for the identification of cations in mixtures. The outstanding value of the ring-oven method seems to be that it can be used for solving special problems, mainly for testing minerals and alloys with minimum amounts of test material. For details, refer to the original work (332).

O. Substoichiometry in Bismuth Analysis

The substoichiometric method of trace analysis, initially developed by Ruzicka and Stary (275) has now been extensively employed. This new method eliminates the necessity of determining the chemical yield of the separation procedures. In addition, it increases substantially the selectivity of the chemical separation, and thus reduces the number of separation steps involved. Substoichiometric determinations can easily be automated, which permits the analysis of a large number of samples with little attention and with minimal handling of radioactivity (276).

The theory and principle of the substoichiometric method of analysis have been described vividly by Ruzicka and Stary in their recent monograph (277) and in several papers (275; 278; 302).

Ruzicka and coworkers (301) studied systematically the effect of pH on the extraction of bismuth using a substoichiometric amount of dithizone in CCl_4 and examined the reproducibility of this substoichiometric extraction of bismuth with dithizone at a pH of about 4.0. They were able to demonstrate from this experiment the agreement of the theory with the actual experimental data.

The course of a substoichiometric determination by neutron activation analysis is very simple. This is done as follows: (1) Standard and test samples are irradiated simultaneously under the same condition. (2) Samples and the standard are dissolved, and exactly the same amount of the carrier is added to each solution. (3) All the solutions are separately and simultaneously extracted under the same conditions with a proper organic reagent (*e.g.*, dithizone, 8-quinolinol, etc.) in a suitable organic solvent. The quantity of the reagent added must be smaller than the quantity corresponding stoichiometrically to the total carrier present, and must be exactly the same in all solutions. In the case of an ion-exchange separation of a water-soluble chelate, complexing agents such as EDTA and related compounds are used and the chelate formed is separated on a cation-exchange column. (4) Finally, the induced radioactivity of exactly equal volumes of extracts (in the case of a solvent extraction) or eluates (in the case of an ion-exchange separation) are measured under the same conditions, and the quantity of the test element is calculated according to the equation developed by Ruzicka and Stary (277).

The determination of traces of metals by 'isotope-dilution analysis' is more simple and rapid according to Ruzicka and Stary than by neutron-activation analysis, because the test samples need not be irradiated in a nuclear reactor.

A selective radiochemical separation of bismuth based on its extraction as the dithizonate from a cyanide solution has been described by Ruzicka, Zeman, and Obrusnik (278). From this cyanide medium only In, Pb, Tl, and Sn are simultaneously extracted. After stripping the organic extract with dilute HNO_3 and adjusting the pH to about 5, bismuth is selectively extracted with a substoichiometric amount of dithizone. The determination of bismuth in granite is an example of this approach.

IV. DISSOLUTION OF BISMUTH SAMPLES

Bismuth is readily dissolved in HNO_3 and presents no special problems. Hydrochloric acid alone will not dissolve bismuth easily, but a mixture of HCl and HNO_3 in the proportion of between 1 : 4 and 3: 4 will dissolve the metal. Its tendency to hydrolyze and precipitate as basic salts requires that its solution be kept fairly acidic. Unlike arsenic and antimony, there is no danger of loss of bismuth by volatilization of its chloride (319). On the other hand, bismuth oxide (Bi_2O_3) can be dissolved in HCl alone and HNO_3 is not required. The presence of tartrate, citrate, or other complexing agents prevents the hydrolysis of bismuth even at low acidity and increases the selectivity of its determination.

Nitric acid digestion is a suitable treatment for many ores and metallurgical products. In the case of Sn-containing alloys, the precipitated metastannic acid may occlude some bismuth and will require an alkaline fusion to ensure that all the bismuth is in solution. The same applies when H_2SO_4 is used in a preliminary attack on Pb-containing alloys, as the precipitate of $PbSO_4$ always carries down small amounts of bismuth (223).

To dissolve oxide minerals the ore sample is extracted for one hour with a solution of 5% thiourea in 0.5-N H_2SO_4. The residue is separated by filtration and washed twice with acidic water and twice with water. The filtrate is treated with tartaric acid, Complexon III, and ammonium hydroxide, and then is analyzed for bismuth (216). The residue is washed twice with 0.2-N HNO_3, calcined at 400°C, treated with HNO_3-HF or HCl-HNO_3 mixture, and analysed for bismuth.

Lead containing bismuth alloys are treated as follows: If the lead content is small, the alloy is treated with HCl + HNO_3 mixture in the proportion of

4 : 1. But if the amount of lead present is large, the alloy is treated with 1 : 5 HNO_3. If the alloy contains tin or antimony, it is dissolved in Br_2 - HBr mixture.

In the case of sulfide minerals the sample is first treated with Br_2 + KBr mixture; after some time, HNO_3 is added and the solution is evaporated to dryness. It is then treated with HCl and H_2SO_4 in the proportion of 1:2 and evaporated to fumes of SO_2. The solution is then diluted with water to a volume of about 50 ml and filtered. The filter paper is finally washed with 1 : 10 H_2SO_4. Some of the minerals are fused with sodium carbonate, or sodium peroxide and sodium hydroxide, and leached with water.

For bismuth in the presence of organic matter or in organic compounds, dry ashing can sometimes be used, followed by dissolution in HNO_3. The usual wet-oxidation procedures are more generally applicable, and digestion with HNO_3 alone (223) has an advantage in that no other anion (*e.g.*, sulfate) is introduced. In certain complex mixtures organic matter associated with bismuth may be destroyed by treatment with H_2SO_4-H_2O_2, or with HNO_3-$HClO_4$.

When bismuth is to be separated from lead cyclotron targets, Pb is easily dissolved in 6-M HNO_3. Occasionally, lead dioxide is used as a target and it can be dissolved in HNO_3 by dropwise addition of hydrogen peroxide.

V. COUNTING TECHNIQUES

The bismuth isotopes ^{199}Bi, ^{200}Bi, ^{201}Bi, ^{211}Bi, ^{212}Bi, ^{213}Bi, ^{214}Bi, ^{215}Bi are short-lived (see Table I), and hence are not convenient as tracers in radiochemical work. On the other hand ^{207}Bi and ^{210}Bi(RaE) are very conveniently obtained and used as tracers. Described below are the counting techniques for these and some other isotopes of bismuth. (See refs. 108; 137; and 218).

A. ^{205}Bi ($t_{1/2}$ = 15.3d)

^{205}Bi decays mainly by electron capture followed by gamma-ray emission. A weak (0.06%) positron group with end point energy of 0.98 MeV is present. The gamma-ray spectrum is somewhat complex, but some prominent gamma rays at 0.571 MeV (14%), 0.703 MeV (28%) and 1.766 MeV (27%) can conveniently be determined with a sodium iodide scintillation or a Ge(Li) semiconductor detector. X-ray counting can also be employed.

B. ^{206}Bi ($t_{1/2}$ = 6.24d)

^{206}Bi also decays by electron capture with the emission of lead x-rays and a complex gamma-ray spectrum. The gamma-ray spectrum can be resolved with a Ge(Li) detector system. Most convenient gamma rays are those of 0.516 MeV (46%), 0.803 MeV (99%), 0.881 MeV (72%), and 1.72 MeV (36%).

If the sample is free from chemical impurities of lead and other neighboring elements, x-ray counting of ^{206}Bi may be very convenient, with a high-resolution Ge(Li) or Si(Li) x-ray detector system with negligible dead layer.

C. ^{207}Bi ($t_{1/2}$ = 30y)

^{207}Bi is a very convenient isotope for tracer studies. It is used as a gamma-ray energy standard for calibration in the nuclear spectroscopic studies of other nuclides.

It decays by electron capture, producing lead x-rays and well-known gamma rays of energies 0.5697 MeV (98%), 1.064 MeV (77%), and 1.770 MeV (9%). These gamma rays can be determined with a NaI(Tl) scintillation spectrometer; a well-type detector is especially useful for liquid samples. Since the gamma rays can be very easily resolved from each other using a scintillation detector and a multichannel pulse height analyser, disintegration rates of samples can be determined rapidly and accurately. Corrections other than for geometry are small and easily made.

An even more accurate method of counting ^{207}Bi is by using a Ge(Li) gamma-ray spectrometer. Large volume detectors now available are excellent because of their high photopeak efficiency and good resolution (Fig. 16). These detectors can be calibrated with standard sources* for their absolute efficiency. The relative efficiency as a function of energy can be determined employing sources which have gamma rays of various energies with known relative intensities. Calibration procedures are described in ref.75 and in refs. a. and b. of Table I, p. 7.

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*A mixed radionuclide, gamma-ray emission-rate, point-source standard for calibration of the energy scale and the absolute detection efficiency of gamma-ray spectrometers as a function of energy is available in two source intensities from the Radioactivity Section, National Bureau of Standards, Washington, DC 20234.

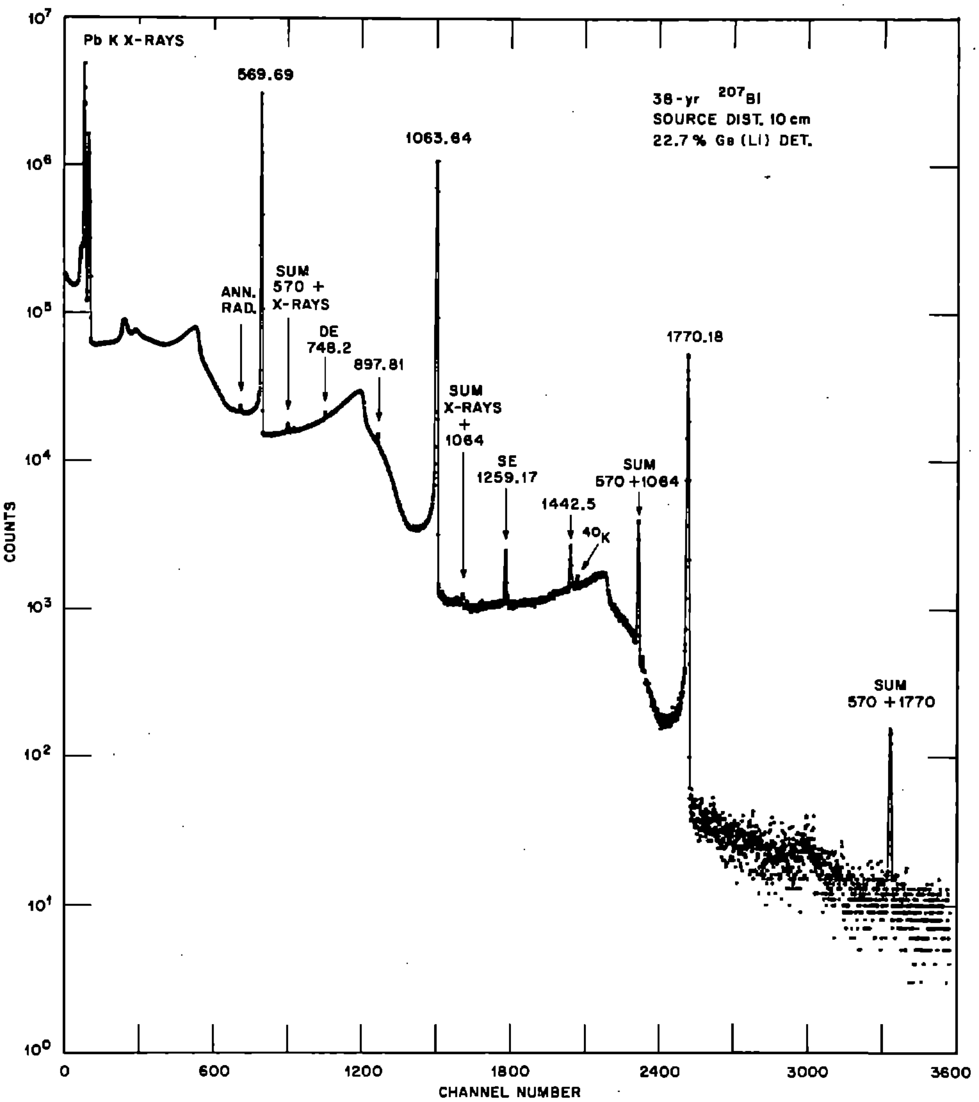

Fig. 16. Gamma-ray spectrum of ^{207}Bi on a large-volume Ge(Li) semiconductor radiation detector. Energies are in keV. Single-escape and double escape peaks are indicated by SE and DE, respectively. (J. S. Eldridge, Oak Ridge National Laboratory).

With the availability of very high resolution Ge(Li) and Si(Li) x-ray detectors, qualitative and quantitative measurements on ^{207}Bi can also be made. However, samples for measurement with such detectors should be free of any inactive Pb or Bi; otherwise, fluorescent x-rays produced in the sample will affect the accuracy of these measurements. Chemical impurities other than Pb and the neighboring elements will not interfere seriously, because the energy resolution of these spectrometers is sufficient to resolve x-rays of neighboring elements. The x-ray spectrometer can be calibrated using standard sources (62) or by using a standard source of ^{207}Bi.

D. ^{208}Bi ($t_{1/2} = 3.7 \times 10^5 y$)

^{208}Bi is a pure electron capture isotope with emission of lead x-rays and a 2.614-MeV (100%) gamma ray. The gamma ray can be counted by a scintillation or Ge(Li) detector. X-ray counting using a solid state x-ray counter is also suitable.

E. ^{210}Bi (RaE, $t_{1/2} = 5.01d$)

^{210}Bi can be produced conveniently by neutron activation of natural bismuth, since ^{209}Bi is 100% abundant. The ^{210}Bi is a beta emitter with an end-point energy of 1.16 MeV (100%). This beta component can easily be measured with a proportional or G.M. beta counter. A thin aluminum absorber should be used to stop all the alpha particles from the daughter nuclide, ^{210}Po ($t_{1/2}$ = 138d). A correction for the absorption in the aluminum absorber should be applied. If the sample is not thin enough, correction for self-scattering and self-absorption also must be made (237).

Measurement of ^{210}Bi can also be achieved by counting the 5.3-MeV alpha particles from its daughter, ^{210}Po (73). The polonium alpha radioactivity is readily determined with a 38 mm diameter, NE 840c ZnS (Ag) scintillator disc, optically coupled to an EMI 6097A photomultiplier. As an example of such a measurement, De Boeck, Adams, and Hoste (73) used a 30 mm diameter silver foil on which the ^{210}Po was deposited, which in turn was mounted on a stainless steel backing serving as a source holder. To obtain a high geometry, the distance of the foils from the ZnS (Ag) screen was only about 2 mm.

De Boeck, Adams, and Hoste (73) used a 1 cm^2 silicon surface-barrier detector to check the identity and purity of the separated alpha activity. Only the ^{210}Po 5.30 MeV alpha peak could be observed. These ^{210}Po samples were not very useful for assay by alpha spectroscopy, owing to the inhomogeneous distribution of polonium on the silver foils.

VI. COLLECTED RADIOCHEMICAL PROCEDURES

Procedure 1

Nuclide Separated: ^{210}Bi (RaE)
Parent Material: ^{210}Pb or its precursors
Type of Experiment: From natural radioactivity
Procedure by: Prestwood (255).
Time of Separation: About 45 minutes
Reagents Required:

- Bismuth carrier-10 mg Bi/ml, as $Bi(NO_3)_3 \cdot 5H_2O$ in 1-M HCl, standardized (Note 1).
- Rhodium carrier - 10 mg Rh/ml as $RhCl_3 \cdot 4H_2O$ in dilute HCl.
- Ruthenium carrier - 10 mg Ru/ml, as $RuCl_3$ in dilute HCl.
- Silver carrier - 10 mg Ag/ml, as $AgNO_3$ in water or dilute HNO_3.
- Tellurium (IV) carrier - 10 mg Te/ml, as Na_2TeO_3 in dilute HCl.
- Other reagents - 1-N,3-N, 6-N, and conc. HCl, conc. $HClO_4$, and NH_4OH; solid $N_2H_4 \cdot H_2SO_4$, NaI, and $NaNO_2$; SO_2 and H_2S gases; hexone (4-methyl-2-pentanone) and methanol (anhydrous).

Yield: ~65%
Degree of Purification: Excellent; sufficient for nuclear spectroscopy
Advantage: Proved extremely effective for the removal of lead

Procedure:

1) To 2.0 ml of Bi and 1 ml of Te(IV) carriers in a 125-ml Erlenmeyer flask, add an aliquot of the sample. Place on a hot plate and evaporate just to dryness. Add 5 ml of conc. HCl and again evaporate to dryness. (Evaporation is necessary to insure Te exchange and also to remove NO_3^-, which inhibits reduction of Te to metal.) Add 15 ml of 3-N HCl and about 100 mg of $N_2H_4 \cdot H_2SO_4$. Heat to boiling on a hot plate and add saturated aqueous SO_2 periodically while the solution is boiling, until all the Te is precipitated as metal and the solution has no blue tinge. (This may take as long as 10 min., with SO_2-water being added at about 2-min intervals). Filter and collect the filtrate in a 40-ml conical centrifuge tube. Rinse the Erlenmeyer flask with hot, 3-N HCl containing SO_2-water and pass the solution through the filter into the centrifuge tube.
2) To the filtrate add conc. NH_4OH to precipitate $Bi(OH)_3$. Centrifuge and discard the supernate (Note 2).
3) To the precipitate add 10 drops of 6-N HCl, 5 drops of Rh carrier, and stir to dissolve. Wash the sides of the centrifuge tube with 2 to 4 ml

of H_2O and heat on a steam bath. (The solution at this point should be clear.) Add 30 ml of boiling H_2O and digest for 5 min, to precipitate BiOCl. Centrifuge the BiOCl precipitate and discard the supernate.

4) To the precipitate add 2 ml of conc. $HClO_4$ and 5 drops of Ru carrier, and with vigorous stirring heat to fumes. Fume until all the RuO_4 has been volatilized and then allow the solution to cool.
5) Add 10 drops of Ag carrier, dilute to 20 ml with H_2O and then add 2 ml of 6-N HCl with vigorous stirring. Centrifuge and transfer the supernate to a clean centrifuge tube containing 5 ml of conc. NH_4OH, to precipitate $Bi(OH)_3$. Centrifuge and discard the supernate.
6) Add 5 ml of 6-N HCl to the $Bi(OH)_3$ precipitate and transfer the solution to a 60-ml separatory funnel. Wash the centrifuge tube with 10 ml of 6-N HCl and add the washings to the separatory funnel. Add 15 ml of hexone and shake vigorously. Drain the H_2O layer into a clean separatory funnel. Add 10 ml of hexone, 1 to 2 g of solid NaI, shake, and discard the H_2O layer. Add to the hexone layer 10 ml of 6-N HCl containing approximately 1 g of NaI. Shake and discard the H_2O layer. To the hexone phase add 10 ml of 6-N HCl and approximately 1/2 g of solid $NaNO_2$ and swirl. Place the stopper in the separatory funnel and shake vigorously. (At this point the aqueous layer is essentially colorless and the hexone phase may be slightly yellow.) Drain the H_2O layer into a clean 40-ml centrifuge tube containing 5 ml of conc. NH_4OH. Centrifuge and discard the supernate.
7) To the $Bi(OH)_3$ precipitate add 10 ml of 3-M HCl and 10 ml of H_2O. Place on a steam bath and saturate with H_2S for at least 2 min. Centrifuge and discard the supernate. Dissolve the Bi_2S_3 precipitate by boiling in 5 ml of 6-N HCl.
8) Precipitate $Bi(OH)_3$ as in step 2.
9) Repeat steps 3, 4, and 5.
10) Transfer the $Bi(OH)_3$ precipitate with 15 ml of 6-N HCl to a 60-ml separatory funnel. Repeat step 6 from "Add 10 ml of hexone, 1 to 2 g of ..."
11) Repeat step 7.
12) Repeat step 2 and then step 3, the latter in the absence of Rh holdback carrier.
13) Filter the BiOCl on to a weighed No. 42 Whatman filter circle, using a ground-off Hirsch funnel and filter chimney. Wash the precipitate with H_2O and then with methanol. Dry at 110° for 5 min, cool for 20 min., weigh, and mount for counting.

Notes:

1) The weight of $Bi(NO_3)_3 \cdot 5H_2O$ employed in the standardization corresponded (by calculation) to 10.0 mg of Bi/ml, whereas the actual standardization as BiOCl showed 10.1 mg Bi/ml.

2) In the event large quantities of Pb activities are present in the sample, they may be removed in the following manner at this stage of the procedure. To the $Bi(OH)_3$ precipitate add 5 drops of Pb carrier, 2 ml of 12-N NaOH, and boil with vigorous stirring. Add 20 ml of H_2O and continue boiling for 3 to 5 min. Centrifuge and discard the supernate, which contains the Pb as plumbite. This procedure has proved extremely effective for the removal of lead.

Preparation and Standardization of Carriers:

Bismuth carrier - Dissolve 23.21 g of $Bi(NO_3)_3 \cdot 5H_2O$ in 1-N HCl, make up to 1 liter with the acid, and filter. Pipet 10.0 ml of the solution to a 250-ml Erlenmeyer flask, add 200 ml of boiling H_2O, and digest overnight on a steam bath. Filter into a weighed 15-ml, sintered-glass crucible of medium porosity. Wash the BiOCl precipitate with H_2O and then with methanol. Dry at 110° for 15 min, cool and weigh. Four standardizations gave a total spread of 0.2% (see note 1, above).

Rhodium carrier - Weigh out 27.34 g of $RhCl_3 \cdot 4H_2O$ and make up to one liter in 0.01 M HCl.

Ruthenium carrier - Dissolve 26 gm of commercial ruthenium chloride (a mixture of the hydrated trichloride and tetrachloride) in one liter of 0.1-N HCl.

Procedure 2

Nuclide Separated: ^{212}Bi (carrier-free)
Separated from: ^{228}Th and its decay products
Type of Experiment: A milking procedure from natural radioactivity
Procedure by: Bhatki *et al.*, (30)
Time of Separation: <30 min
Reagents Required: Dilute hydrochloric acid (0.5 N and 1.5 N); Dowex-50W X 8 resin (100-200 mesh); and other bench reagents such as HCl, NH_4Cl, etc.
Yield: Quite high, (>90%)
Degree of Purification: Sufficiently good for tracer work, see Figs. 17, 18.
Advantage: The procedure is fast and very effective for the separation from ^{212}Pb, ^{228}Th, and other decay products of radiothorium.

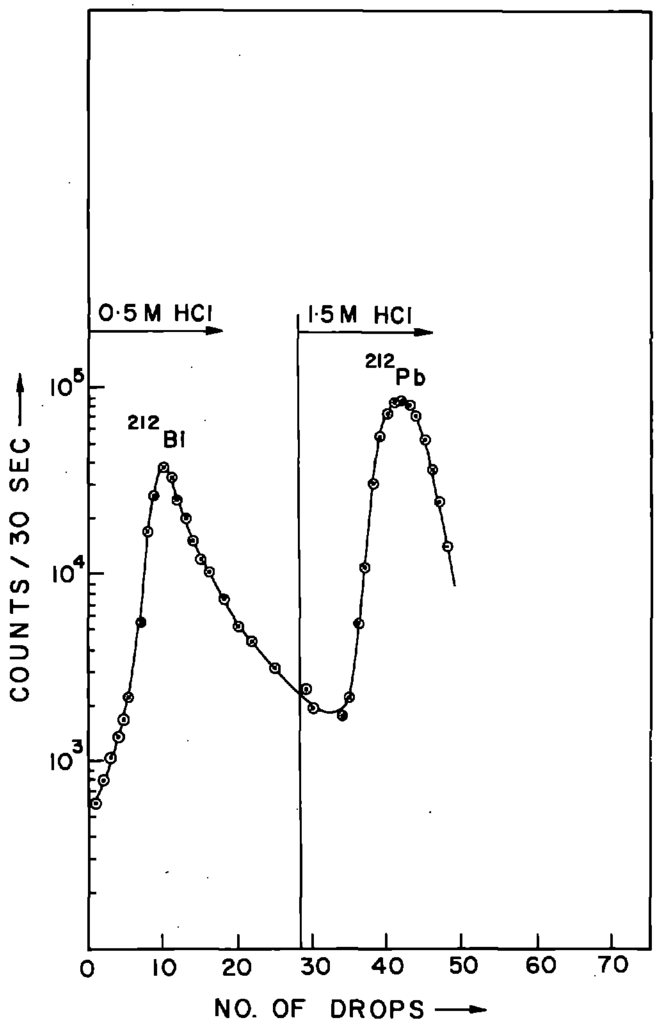

Fig. 17. Elution curves for ^{212}Bi and ^{212}Pb using cation exchange resin and dilute HCl as described in Procedure 2.

Procedure:

1) Prepare a cation exchange resin column using glass tubing of ~5 mm internal diameter, so that the height of the resin in the column is about 40 mm.
2) Cycle the resin through hydrogen and ammonium forms using bench HCl and NH_4Cl solutions, and finally leave the resin in the hydrogen form.
3) Rinse the resin with distilled water.

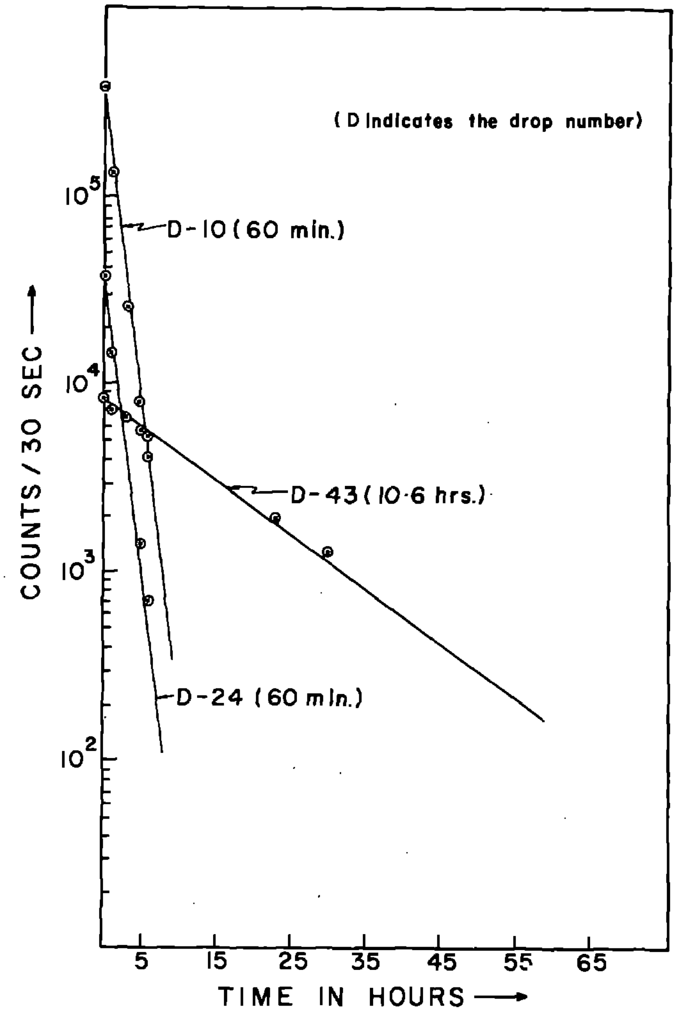

Fig. 18. Decay curves of particular fractions collected during the elution portrayed in Fig. 17. The half-lives of 60 min and 10.6 hrs are characteristic of ^{212}Bi and ^{212}Pb, respectively.

4) Adsorb the ^{228}Th activity (Note 1) on the resin column using a minimum volume of ~1-N HCl.
5) Rinse the column with water, and allow ^{212}Bi activity to grow (~3 hrs, Note 2).
6) Elute the ^{212}Bi activity by passing 0.5-N HCl through the column at the rate of one drop per 15 to 20 sec.
7) Collect the drops in the planchets, one drop in each.

8) If ^{212}Pb is also required, change the eluent to 1.5-N HCl after the collection of 25 to 30 drops of 0.5-N HCl, and collect some 25 drops more (Note 3).
9) Evaporate the collected drops in the planchets under an infrared lamp.
10) Count each planchet for 30 sec on a scintillation spectrometer to determine gamma-ray activity.
11) Repeat the gamma-counting at fixed intervals, under the same geometry (Note 4).
12) Plot elution curves (drop number against counting rate) as shown in Fig. 17.
13) Rinse the column with distilled water and keep it ready for the next milking.

Notes:

1) The ^{228}Ra (MsThl) was acquired from Harwell (England). ^{228}Th was separated from it employing Dowex-50W X 8 cation exchange resin, using a procedure similar to that described by Bhatki and Adloff (29).
2) If ^{212}Pb is not removed from the column, the ^{212}Bi activity will grow to the extent of 87% in three hours time. It is preferable to adsorb ^{228}Th the previous evening, and to start the milking of ^{212}Bi tracer (the 60.5-min daughter of the 10.6 hour parent, ^{212}Pb) the next morning. Two to three milkings in good yields of the ^{212}Bi tracer activity can be achieved on each working day of eight hours.
3) For milking of ^{212}Bi only, step 8 is not required, and one can proceed with steps 9 to 13 without step 8. But in case ^{212}Pb is also required and is eluted with 1.5-N or 2-N HCl, it will be necessary to wait for 24 hrs for ^{212}Pb to grow to sufficient intensity for milking.
4) An automatic sample changer similar to that sold by Nuclear Chicago Corporation, U.S.A., for counting twenty-planchets, would be advantageous for this type of work.

Remarks:

It is seen from Figs. 17 and 18 that excellent separation of ^{212}Bi from ^{212}Pb is possible using 0.5-N HCl to elute bismuth activity. The half-life measurements for drop numbers 10 (bismuth peak point) and 24 (just before the lead peak began) showed the purity of bismuth obtained (Fig. 18). However, it should be mentioned that all drops beyond drop number 20 showed traces of ^{212}Pb when counted the next day, after the decay of all ^{212}Bi. However, the drops below number 20 did not show any activity above background the next day, indicating the absence of any appreciable contamination of ^{212}Pb.

Procedure 3

Nuclide Separated: ^{212}Bi (ThC)

Material: Thorium nitrate (old sample)*: natural source.

Procedure by: Harrison, Lindsey and Phillips (128).

Time of Separation: Less than one hour.

Degree of Purification: Excellent

Advantages: Fast and simple procedure

Reagents: Thorium nitrate, standard bismuth solution (see p. 107), electroplating apparatus, 0.5-N HCl, ethyl alcohol.

Procedure:

1) Weigh out about 1 g of thorium nitrate, which is in equilibrium with its daughters. (See remark.)
2) Dissolve in 20 to 25 ml of 0.5-N HCl.
3) Pipette out the requisite volume of the standard bismuth solution ($\geq$ 0.2 mg Bi) into the solution to be electrolysed.
4) Heat the solution in a water bath to 80-90°C.
5) Clean the platinum electrodes. Insert them and a calomel half-cell into the solution to be electrolysed.
6) Start the stirrer, and switch on the current.
7) Increase the current until a potential of 0.25-0.30 V relative to the saturated calomel electrode is attained.
8) Continue the plating for about 25 minutes.
9) Withdraw the cathode with the deposit of ^{212}Bi (ThC), while the current is still on.
10) Wash the cathode with little distilled water, then with alcohol and dry.
11) The cathode is now ready for counting (see also Procedure 14).

Notes:

1) If ^{212}Pb(ThB) is also to be recovered from this solution of thorium nitrate, then introduce a fresh cathode into the electrolytic cell. Increase the current to about 0.15 amps cm^{-2} (with no controlled potential employed), and continue the deposition for 10-20 minutes. Remove the cathode with the current left on, rinse it with water, then with alcohol, and dry.
2) A nickel cathode is also suitable.

*Remark:

Old thorium nitrate is not very essential, as even freshly-manufactured, natural thorium salt will give virtually maximum activity due to the retention during manufacture of the 1.9-y ^{228}Th at the equilibrium concentration present in the original ore.

Procedure 4

Nuclide Separated: ^{210}Bi (RaE)

Separated from: ^{210}Pb (RaD) and other impurities such as Po, Pt, and Au.

Procedure by: Warren and Fink (330)

Time of Separation: Less than 30 minutes

Degree of Purification: Decontamination factor greater than 10^6

Advantages: Simple and fast separation method with exceptionally high mutual decontamination factors.

Reagents: Chemically pure n-butyl phosphate and acetone; paper chromatography apparatus; Eaton-Dikeman Grade 320 industrial paper, 2.5 or 1.5 mm thick.

Procedure:

1) The glass tube is placed erect in a beaker or a beaker inside a tube (pp. 73-75) containing 80% acetone - 20% n-butyl phosphate and the top sealed with a cork or rubber stopper fitted with a glass hook or a clip to serve as a paper holder.
2) The tube is saturated with the developer vapors by immersing a purified paper strip (see Note 1) in the mixed solvent and suspending it from the hanger for 20 minutes prior to introduction of the sample.
3) Although the separation works best carrier-free, carrier in concentration not greater than 5 x 10^{-5} g cm^{-1} of paper width may be added to the sample.
4) Evaporate the sample to dryness, dissolve the residue in water, and adjust the volume such that one ml of solution will be distributed over a minimum 10-cm width of paper.
5) Apply the solution evenly across the width of the paper strip with a micro-pipet (see Note 1), about 3 cm from the end.
6) Suspend the strip from the glass hook or the clip so that the end of the paper is just immersed in the developer. Separations are obtained after the solvent front has travelled more than 18 cm (less than 30 minutes).

7) Remove the paper strip and identify the various zones. The normal R_f values (the ratio of the distance travelled by a component to the distance travelled by the solvent front) (p. 75) are: $Au^{3+} = 1.0$; $Hg^{2+} = 0.90$; $Po^{4+} = 0.80$; $Pt^{4+} = 0.5$; $Tl^{3+} = 0.05$; $Bi^{3+} = 0.60$ and $Pb^{2+} = 0.00$ (*i.e.*, Pb remains at the point of application).
8) The desired zones are clipped from the strip and the cations extracted by boiling with aqua regia, extracted with an organic solvent, or extracted with a solution of a chelating agent in an organic solvent. (36; 137).

Notes:

1) The Eaton-Dikemann Grade 320 Industrial Paper was purified by downward percolation with 1-N HCl and rinsed by downward percolation with water.
2) In order to insure ready identification of the components (except Po) whose concentrations are very low or carrier-free, a simultaneous calibration run with an inactive mixture of the same components may be made on an unused portion of the same paper. An alternative method is to spot each component separately using KI as a streak reagent. In the calibration run, concentrations are high enough to permit detection with streak reagents. Radioactive zones will be in the same relative positions as the inert zones.
3) Each zone may be identified by streaking with the following three reagents: (a) 10% KI; (b) 1% solution of diphenyl carbazide in alcohol; (c) 0.05% solution of benzidine in 10% acetic acid.

Procedure 5

Nuclide Separated: ^{212}Bi (ThC) from ^{212}Pb (ThB) parent.

Material Employed: Natural $Th(NO_3)_4 \cdot 4H_2O$. (See Remarks)

Procedure by: Sill and Willis (292).

Advantages: The processed thorium solution can be used daily for milking of ThC from ThB.

Reagents: Concentrated HCl and $HClO_4$ (72%); Diethylammonium-diethyldithiocarbamate, chloroform, $NaHSO_4$ solution (50%) and conc. HNO_3.

Procedure:

1) Place 200 g of reagent-grade thorium nitrate and 110 ml of 72% perchloric acid into a 600-ml beaker.
2) Heat the mixture on a hot plate until all the solid has dissolved with the evolution of NO_2 and subsequently heavy white fumes.

3) Continue the evaporation of the excess $HClO_4$ until the froth at the surface of the solution tends to crust over while still on the hot plate.
4) Cool the solution, and add 20 ml of 72% $HClO_4$ and 400 ml of water.
5) Boil the solution gently for a few minutes to dissolve the cake and to volatilize decomposition products of $HClO_4$ and cool. (Note 1).
6) Transfer the solution to a 500-ml separatory funnel and shake vigorously with 20 ml of a 1% solution of diethyl-ammonium diethyldithiocarbamate (DDTC) in chloroform for at least one minute.
7) Draw off the extract into a 250-ml separatory funnel containing 100 ml of water and 10 ml of $HClO_4$ (72%).
8) Repeat the extraction with another 10 ml portion of the 1% DDTC in chloroform.
9) Add this extract to the separator containing the first one and shake the funnel vigorously for one minute to wash the combined extracts.
10) Draw off the organic phase into a 250-ml Erlenmeyer flask.
11) Add 2 ml of 50% $NaHSO_4$ solution and 2 ml of conc. HNO_3 to the combined extracts.
12) Heat carefully on a hot plate until the chloroform has evaporated.
13) Continue heating till the charred mass is completely dry.
14) Cool, and add 3 ml of a 1 : 1 mixture of conc. HNO_3 and 72% $HClO_4$.
15) Boil until the black suspension becomes colorless and excess $HClO_4$ has evaporated.
16) Add 10 ml of water and 1 ml of conc. HCl, and boil for 1 minute.
17) Cool and dilute to 10 ml (Note 2).
18) Use this ^{212}Pb tracer as a source of ^{212}Bi. (See Remarks 5).

Notes:

1) The solution at this stage will be about 0.7-N in $HClO_4$ and 450 ml in volume.
2) Each milliliter of this solution will contain approximately 8.5×10^5 cpm of the ^{212}Pb tracer ($t_{1/2} = 10.6$ hr).
3) Wash the original thorium aqueous extract with 20 ml of pure chloroform for one minute to clean up the remaining traces of DDTC, so that the solution is ready for another milking, the next day.

Remarks:

1) 200 g of a thirteen year old thorium nitrate sample yields approximately 8.5×10^6 cpm of ^{212}Pb tracer under the conditions described.

2) From this used up thorium nitrate aqueous phase, 75% of the ^{212}Pb tracer will be regenerated within 21 hours.
3) See remark following Procedure 3.
4) The gamma-ray spectrum of thorium nitrate solution taken on a 7.6-cm NaI(Tl) spectrometer immediately after removal of lead tracer shows only ^{228}Ac (see Fig. 19), and no trace of other decay products such as

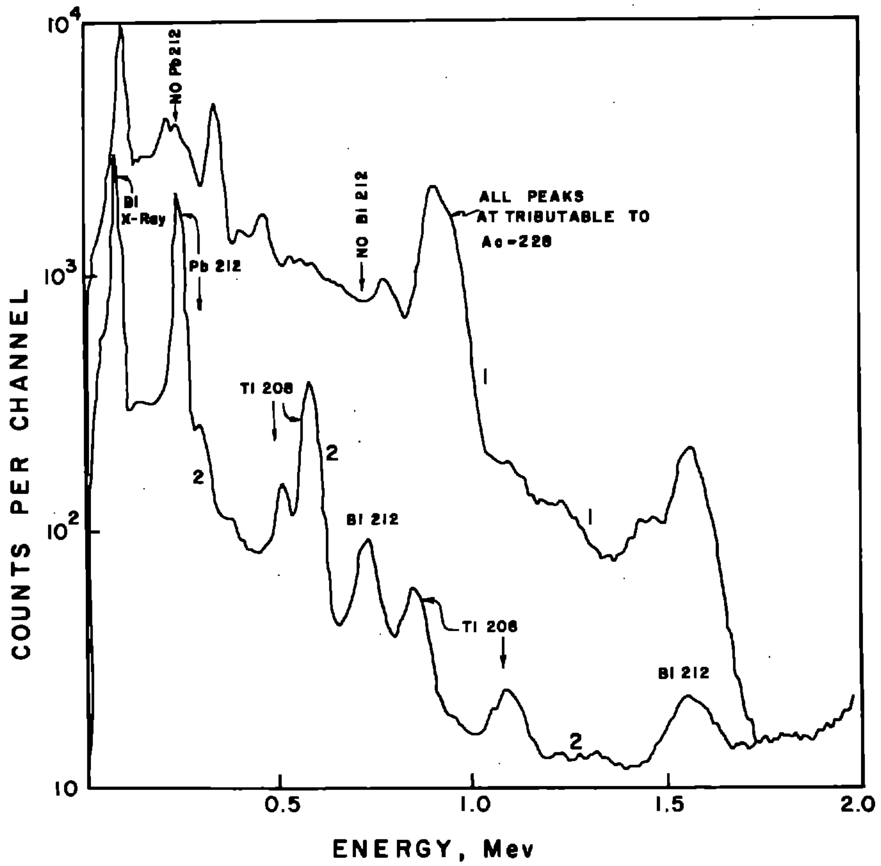

Fig. 19. Gamma-ray spectra for (1) aqueous and (2) organic extracts obtained from thorium nitrate and diethyldithiocarbamate solutions (see Procedure 5). Ref. 292. Reproduced by permission; see p. 128.

^{212}Pb, ^{212}Bi, and ^{208}Tl, which are removed. The lower curve shows a spectrum of the DDTC extract, which includes the complete spectrum of ^{212}Pb, ^{212}Bi, and ^{208}Tl, which existed in the original sample of thorium nitrate.
5) This ^{212}Pb tracer is employed for miling ^{212}Bi, either by Procedure 2

(cation exchange), or by an anion-exchange procedure employing dilute HCl or pure water.

Procedure 6

Element Separated: Bismuth daughter nuclides
Parent Material: Polonium in 20% tributyl phosphate, 80% dibutyl ether
Type of Experiment: A milking procedure
Procedure by: Karraker (212).
Time of Separation: ∿5 minutes
Equipment Required: Standard
Yield: 95-100%
Degree of Purification: Factor of 10^6 from polonium with two washes
Advantages: Simple and fast

Procedure:

To milk solution:

1) Extract mixture of 20% tributyl phosphate, 80% dibutyl ether with an equal volume of 6-N HCl. Bismuth and Pb go into aqueous phase. (Separate Tl as given in steps a-d, below).
2) Wash HCl extract twice with 1/10 its volume of tributyl phosphate solvent. Add the first portion to the polonium solution, and discard the second portions.
3) Add 0.5 mg each of Pb and Bi carriers (Note 1).
4) Add ammonia dropwise to this solution until a permanent precipitate just forms, and then add HNO_3 dropwise until solution just clears.
5) Dilute the solution to about 45 ml and heat in a water bath for a few minutes. Fine crystals of BiOCl should form.
6) Centrifuge BiOCl.

Separate the thallium daughters from lead as follows:

a. To the 6-N HCl solution add 3 to 4 drops of $KMnO_4$ solution to insure oxidation of $Tl^+ \rightarrow Tl^{3+}$. Stir solution until loss of brown color.
b. Add 10 ml of HCl-saturated diethyl ether; (Note 2). Stir for about 3 min and centrifuge.
c. Remove the ether layer containing Tl^{3+}.
d. Repeat the extraction a second time, if necessary.

Notes:

1) Thallium carrier may be added if desired, but is not necessary.
2) The HCl-saturated ether can be conveniently prepared by shaking ether

with conc. HCl and allowing the two layers to stand in contact until ether is needed.

Procedure 7

Parent Material: Tracer ^{228}Pa and daughters

Type of Procedure: Milking experiment

Procedure by: Meinke (212).

Time of Separation: ∿1-1/2 hours

Reagents Required: Thenoyltrifluoroacetone (TTA) solution in benzene; bismuth carrier solution (Procedure 1); lead carrier solution; 6-N HCl; ammonium sulfate (bench reagent), and H_2S.

Yield: ∿60%

Degree of Purification: Decontamination factor of at least 10^3 from Pa and at least 100 from other activities. Factor of at least 5 from Pb.

Disadvantages: Gives a thick sample, poor for alpha spectrometry

Procedure: Previously purified tracer ^{228}Pa is in benzene - TTA solution.

1) Stir organic layer for 10 minutes with an equal volume of 6-N HCl (daughters extract into the acid layer, but most of Pa remains with the organic layer).
2) Wash the acid layer three times with a double volume of 0.4 M TTA in benzene, stirring 5 min each. (Removes Pa).
3) Dilute the acid layer to ∿2 N, and add ∿1/2 mg Bi as carrier. Bubble in H_2S gas to precipitate Bi and Pb sulfides. Centrifuge.
4) Again add 1/2 mg Bi carrier and repeat sulfide precipitation. Centrifuge and combine precipitates of (3) and (4).
5) Dissolve sulfide precipitates in a few drops of hot, conc. HCl. Dilute to at least 1-N acid and reprecipitate sulfides by bubbling in H_2S. Centrifuge.
6) Repeat step (5) four times.
7) Dissolve the sulfide precipitate in few drops of conc. HCl, dilute to ∿6 ml and boil to rid solution of H_2S.
8) Add 1 mg Pb carrier and precipitate $PbSO_4$ by adding SO_4^{-2} as H_2SO_4, $(NH_4)_2SO_4$, etc. Discard precipitate.
9) Repeat step (8) three times.
10) Add H_2S to supernate from last precipitation and centrifuge out the Bi_2S_3 formed.
11) Dissolve the Bi_2S_3 in hot conc. HCl, dilute to a known volume and

plate aliquot for counting. Caution: do not flame the $BiCl_3$ plate, or much of the activity may be lost.

Procedure 8

Nuclides Separated: ^{204}Bi, ^{206}Bi (carrier-free)
Target Material: Lead foil
Type of Bombardment: 19-MeV deuterons
Procedure by: Gile, Garrison, and Hamilton (111).
Time of Separation: Not mentioned, but estimated at less than 30 minutes
Yield: >95%
Advantages: Simple and straight forward procedure
Reagents: Nitric acid (16 N); NaOH (10%), dilute HCl (6 N)

Procedure:

1) Dissolve the bombarded lead foil in a minimum amount of 16-N HNO_3.
2) Evaporate the solution almost to dryness.
3) Take up the residue in a little water and add NaOH solution in adequate quantity to give a clear solution of sodium plumbite.
4) Dilute the solution with an equal volume of water.
5) Filter the solution through Whatman filter paper to retain radiocolloidal bismuth activities.
6) Wash the filter paper with 5% NaOH solution. (Note).
7) Remove the bismuth activity with 6-N HCl.
8) Count the activity in a suitable container after drying.

Note:

Washing is done til there is a negative reaction for lead in the washings, and then wash with little water.

Procedure 9

Nuclides Separated: ^{206}Bi, ^{207}Bi(carrier-free)
Target Material: Lead
Type of Bombardment: Deuterons or protons from cyclotron
Procedure by: Neirinckx (232).
Equipment Required: Standard
Degree of Purification: Sufficiently pure for nuclear spectroscopy
Advantages: Simple, fast and very effective for the removal of lead.

Procedure:

1) Dissolve the lead target in nitric acid.
2) Dilute the solution so the final concentration of HNO_3 is 0.2 N.
3) Extract with an equal volume of 0.3-M bis(2-ethyl-hexyl) phosphate in heptane solution and separate the extract containing radiobismuth into another clean separatory funnel.
4) Repeat the extract with a fresh portion of the reagent solution in heptane.
5) Combine both the organic extracts and wash them successively with two portions of 0.2-N HNO_3, and separate the phases.
6) The organic phase contains most of radiobismuth in a sufficiently pure form.
7) Back-extract bismuth activity with 9-N HNO_3.
8) Use this solution for preparation of bismuth sources.

Procedure 10

Nuclide Separated: Carrier-free ^{206}Bi
Target Material: Enriched $^{206}Pb(NO_3)_2$
Type of Bombardment: Deuterons from cyclotron
Procedure by: Inarida and Shimamura (141).
Yield: ~95%
Degree of Purification: High radiochemical purity
Advantages: Simple and fast
Reagents: Dilute HNO_3 (0.1 N); 8-hydroxy quinoline (oxine) in TBP (0.2 M, and conc. HNO_3
Equipment: Separatory funnels and other standard equipment

Procedure:

1) Dissolve the bombarded, enriched $^{206}Pb(NO_3)_2$ target in a minimum volume of 0.1-N HNO_3.
2) Add equal volume of 0.2-M oxine in TBP and shake well (~1 min).
3) Separate the organic phase into another clean separatory funnel.
4) Repeat step 2 with the aqueous phase.
5) Combine both the organic phases.
6) Wash the mixed organic phase with 0.1-N HNO_3.
7) Shake the organic phase with conc. HNO_3 to back-extract all radiobismuth.
8) Separate the aqueous acid phase containing ^{206}Bi and evaporate the nitric acid.

9) Treat the solution with HCl and evaporate to a small volume.

Procedure 11

Nuclides Separated: ^{199}Bi, ^{201}Bi, ^{203}Bi, and ^{205}Bi
Target Material: Natural lead
Type of Bombardment: 25-MeV deuterons, or protons up to 70-MeV energy
Procedure by: Stockendal, McDonell, Schmorak and Bergstrom (305).
Time of Separation: Not stated (may be < 1 hour)
Degree of Purification: Excellent
Advantages: Simple procedure and clean separation
Equipment: Jacketed ion-exchange column; ice bath; centrifuge.

Procedure:

1) Dissolve lead target in concentrated nitric acid.
2) Add hydrochloric acid, and cool the solution in an ice bath.
3) Separate the $PbCl_2$ precipitate by centrifugation and decant the supernatant liquid into a clean tube.
4) Boil the solution with addition of conc. HCl until HNO_3 is completely destroyed, and evaporate to a small volume.
5) Dilute with water until the HCl concentration is about 0.3 N.
6) Pass through a jacketed column, heated to 82.3°C by refluxing isopropyl alcohol and packed with Dowex-1 anion exchange resin, 200 mesh. Wash column with 0.3-N HCl, to remove all lead.
7) The Bi isotopes remain firmly adsorbed on the resin, but the Pb is removed. Remove Bi activity by treating the column with HNO_3 (0.5 N) or conc. HCl (12 N). Collect the eluted radiobismuth in a beaker, concentrate to a small volume, and transfer to a suitable container for counting.

Procedure 12

Nuclide Separated: ^{207}Bi
Target Material: Lead-copper alloy
Type of Bombardment: Deuterons or protons
Procedure by: Erlychenko, *et al.*, (86)
Time of Separation: Less than one hour
Equipment Required: Standard
Advantages: A clean separation from lead, copper and zinc
Reagents: Dilute HNO_3 (1 : 1), NH_4OH, dilute HCl, pyridine, and iron carrier 10 mg/ml, Dowex 1 X 8, 100-200 mesh, anion exchange resin.

Procedure:

1) Melt the lead-copper alloy target by heating it to about 400°C.
2) Dissolve it in minimum amount of 1:1 nitric acid and add 1 ml of iron carrier solution containing 10 mg of Fe^{3+}.
3) Dilute the mixture to 100-150 ml.
4) Neutralize the solution with NH_4OH to a pH of about one.
5) Add to this a mixture of 4 ml of 12-N HNO_3, 9 ml H_2O, and 7 ml of pyridine. Bismuth is coprecipitated with $Fe(OH)_3$.
6) Separate the precipitate by filtration or by centrifugation.
7) Dissolve the precipitate in a minimum amount of 1:1 nitric acid.
8) Add HCl and water, so that the final HCl and HNO_3 concentrations are 0.2 and 2 moles per liter respectively.
9) Pass this solution through a small Dowex 1 X 8 anion exchange column in the nitrate form.
10) Remove iron and traces of lead (if any) by washing the column with dilute HCl (0.02 N).
11) Finally remove radiobismuth by eluting it with dilute HNO_3 (0.5 N).

Procedure 13

Element Separated: Bismuth

Target Material: Lead

Type of Bombardment: Protons or deuterons.

Procedure by: Neuman (in 212).

Time of Separation: 15 minutes from solution of target to the plating step

Yield: 65% in 45 minutes. See Remarks.

Degree of Purification: Good separation from lead and thallium: at least a decontamination factor of 10^4. Interference from noble metals.

Advantages: Rapid separation when looking for short half-lives. Prepares carrier-free samples for alpha spectrometry, or high specific activity samples for mass-spectrograph or beta-ray spectrometer studies

Procedure:

1) Dissolve Pb target in 6-N HNO_3. Keep volume as small as possible. Add water if necessary to get complete solution.
2) Add 8-N NaOH dropwise until formation of $Pb(OH)_2$. Add HNO_3 dropwise until solution just clears.
3) Place Ni foil in solution. Bismuth will electrochemically replace Ni

in foil. Keep solution warm, and stir continuously to obtain highest yields. (See Remarks).

4) Counting and alpha spectrometry can be done directly on the Ni foil after washing well and drying. The nickel foil should be given a protective coating (label shellac is satisfactory) on one side so that the activity plates on the unprotected side.
5) To prepare a sample for a mass spectrograph or beta-ray spectrometer, remove the Ni foil from the solution when the desired amount of activity is obtained, and wash well. Dissolve the Ni foil in HNO_3. Add 50 micrograms of Bi carrier and 20 mg of La carrier. Precipitate $La(OH)_3$ and $Bi(OH)_3$ by addition of NH_3. Wash precipitate with water and 1 drop of NH_3. Dissolve in a few drops of HCl, dilute to 0.3-N HCl, and pass H_2S into solution. Bi_2S_3 precipitates. Further disposition of sample depends on type of mounting necessary for instrument.

Remarks:

1) As a rough indication of yields to be expected, a volume of ∿40 ml, heated to ∿85°C, and stirred slowly with mechanical stirrer gives these yields at various time intervals: 5 min, 10%; 15 min, 25%; 45 min, 65%.
2) This procedure does not give separation from metals which are more easily reduced than Bi. Among the spallation-products impurities will be Au, Hg, and Pt metals. Among the fission-product impurities will be Cu, Ag, Pt metals, and Sb. There will be no separation from Po if it is produced in bombardment.

Procedure 14

Element Separated: Bismuth
Separation From: Lead and other activities
Procedure by: Lingane and Jones (192).
Reagents: Tartarate solution (0.25 M) and hydrazine hydrochloride
Equipment: Same as in Procedure 3

Procedure:

1) Clean the platinum cathode.
2) Dissolve the activities in 0.25-M tartarate solution.
3) Add one g of hydrazine hydrochloride per 100 ml of the solution (Note).
4) Adjust the pH to between 5.8-6.0.
5) Start the current and perform the deposition sequentially at the

following voltages: Cu, -0.30 V; Bi, -0.40 V; Pb, -0.60 V. If only bismuth separation is required, carry out the prior deposition at -0.30 V to remove copper, if any.

Note:

Small amounts of Bi and Pb carriers must be present. The amount of each carrier should be in the range 0.05-5 mg. The plating is continued at each step until the current falls to a low and a constant value (109).

Procedure 15

Material Employed: Rocks and minerals

Procedure by: Greenland and Campbell (120).

Reagents Required: Conc. HF; $HClO_4$ (72%); KI; methylisobutylketone, and disodium salt of EDTA.

Advantages: A rapid procedure suitable for the routine determination of nanogram amounts of bismuth in a silicate rock or mineral

Procedure:

1) Dissolve a known quantity of the rock or the mineral in HF-$HClO_4$ acid mixture in the presence of ^{207}Bi tracer.
2) Evaporate the solution to remove silica.
3) Take up the perchlorate residue in water.
4) Extract Bi as the iodide complex into methylisobutylketone.
5) Wash the organic phase three times with acid-iodide solution.
6) Back extract bismuth into the aqueous phase.
7) Treat it with a substoichiometric amount of EDTA.
8) Extract the excess, unreacted bismuth again as the iodide complex.
9) Determine the specific activity of the bismuth-EDTA complex in the aqueous phase.

Procedure 16

Nuclide Separated: ^{210}Po; daughter product of ^{210}Bi

Material Employed: Terrestrial rocks and meteorites

Type of Bombardment: Thermal neutron irradiation $^{209}Bi\ (n,\gamma)^{210}Bi$; Bi is determined by α counting of ^{210}Po

Procedure by: Santoliquido and Ehmann (282).

Time of Separation: 4 hours

Yield: Greater than 90%

Reagents: Conc. H_2SO_4, conc. HF, dilute NH_4OH, hydroxylamine, sodium citrate, SO_2, silver disc (0.08 mm thick), ^{208}Po tracer for chemical-yield determination

Advantages: Simple and fast procedure, clean operation by spontaneous deposition on Ag disc

Preliminary treatment and irradiation:

About 100-300 mg of a sample is weighed into a clean quartz vial and then sealed. Bismuth standard solution is prepared by dissolving high purity Bi metal in concentrated HNO_3 and further diluting with 4-M HNO_3. An aliquot of the standard solution is evaporated onto approximately 200 mg of "Specpure" SiO_2 contained in a quartz vial and sealed. Samples along with Bi standard are irradiated in a reactor for ∿100 hours at a flux of 10^{13} n cm^{-2} sec^{-1}. Then, at least 20 days are allowed to pass between the end of irradiation and the beginning of chemical work, to permit essentially all the ^{210}Bi activity to decay to ^{210}Po.

Procedure:

1) Transfer the irradiated sample to a teflon dish. Pipet a known aliquot of ^{208}Po tracer solution into the dish to serve as an indicator for chemical yield determination.
2) Decompose the sample with conc. H_2SO_4 and HF. Later, add *aqua regia* to dissolve metal grains. Remove the nitrate ions by evaporation, and make up the final solution to 20-50 ml, 1-N HCl. The solution should be clear at this stage. Transfer the solution to a disposable polypropylene beaker.
3) Add 1.0 g of hydroxylamine and 0.5 g of sodium citrate to the solution. Bubble SO_2 for few minutes, and adjust the pH of the solution to 4 with dilute NH_4OH.
4) Clean one side of a silver disc until it is shiny. Cover the back of the disc with epoxy resin. Cement the silver disc with epoxy resin to a teflon rod which is affixed to a stirring motor. Lower the disc into the solution. Maintain the temperature of the solution at about 70°C. Polonium is plated out onto the silver disc in 4 hours.
5) After plating, wash the silver disc with distilled water, dilute NH_4OH, and ethanol. Count it with a surface barrier silicon detector. Tracer ^{208}Po α (5.11 MeV) counting is used for chemical yield. The chemical yields are greater than 90 percent.

Procedure 17

Nuclide Separated: ^{210}Bi
Material Employed: Meteorites, terrestrial and lunar samples
Type of Bombardment: Thermal neutron irradiation
Procedure by: Keays, Ganapathy, Laul, Krähenbühl and Morgan (159)
Yield: 60-70%
Reagents: Anion-exchange resin AG 1-X10, 100-200 mesh, 5% thioacetamide, NaI, $NaNO_2$, Na_3PO_4, methylisobutylketone (MIBK, hexone), dilute NH_4OH, 6-N NaOH, HNO_3 0.1-N, 1-N, 2-N, 6-N and conc. HCl, Ce(IV) solution, Bi carrier (10 mg/ml) and hold-back carriers, 10 mg/ml each of Al, Cd, Co, Cr, Cu, Fe, Hg, Ir, Sb, Se, Te and Zn.
Advantages: Clean Chemistry, suitable for low concentration of Bi in a sample.

Sample Preparation and Irradiation:

A sample is weighed in a cleaned high-purity quartz vial and sealed. About 0.10 g of Bi standard stock solution (0.10 mg/ml) is weighed into a quartz vial, and 20-50 mg of "Specpure" MgO is added. The standard solution is evaporated to dryness in an oven at 70°C, and the vial is sealed. Samples and Bi standard are irradiated together in a reactor at a high flux of 10^{14} $n \cdot cm^{-2}$ sec^{-1} for ∿100 hours. After 2-4 days of cooling, the samples are processed.

Preliminary Treatment of Sample:

The irradiated sample is transferred to a Ni/Zr crucible in which 45 mg of Bi inactive carrier (15 mg/ml), 5 mg of Ir (Note 1), and other elements (if needed) (see 159) are already pipetted, made slightly basic with 6-N NaOH, and dried under a heat lamp. About 5 g of Na_2O_2 and 20 pellets of NaOH are added to the crucible. The mixture is then fused for 15-30 minutes until the melt is clear. The fused mass is cooled and decomposed with H_2O, transferred to a 250-ml beaker, and 5 ml of 10% Na_2S are added. The precipitate containing Bi and other elements is centrifuged and saved.

The precipitate is dissolved in 30 ml of *aqua regia*. The solution is digested on a hot plate and the nitrate ions are removed by successive additions of HCl. The final solution is made up to 20-30 ml in 1-N HCl and filtered. The solution is loaded onto an anion-exchange column, 1 cm x 10 cm (AG 1-X10, 100-200 mesh), pre-conditioned with 1-N HCl-0.004-M Ce(IV) (Note 2). The effluent is discarded. The column is washed successively with 100 ml each of 1-N HCl, 0.1-N HCl, 0.002-N HCl. Bismuth is eluted with 200 ml of 1-M H_2SO_4 containing 0.2% cerium(IV) sulfate. The Bi solution is evaporated to a low volume and Bi_2S_3 is precipitated with 5 ml of 5% thioacetamide. The Bi_2S_3 is centrifuged and saved for further purification.

Final Procedure:

1) Dissolve the Bi_2S_3 in 5 ml of conc. HCl, boil off H_2S and add H_2O to precipitate BiOCl. Centrifuge, and discard the supernate.
2) Add 5 ml of conc. HCl and 2 ml of conc. HNO_3 to the precipitate. Add 5 mg each of Al, Cd, Co, Cr, Cu, Fe, Hg, Ir, Sb, Se, Te and Zn hold-back carriers. Evaporate the mixture to dryness in a water bath. Dissolve the residue in 20 ml of 2-N HCl (filter off any turbidity). Load the solution onto a second anion-exchange column (AG 1-X10, 100-200 mesh), pre-conditioned with 2-N HCl-0.004-M Ce(IV) (prepared immediately before use). Wash the column with 100 ml each of 2-N HCl, 0.1-N HCl, and 0.002-N HCl.
3) Elute Bi with 200 ml of 1-M H_2SO_4-0.2% cerium(IV) sulfate. Reduce the volume on a hot plate and precipitate Bi_2S_3 with 5% thioacetamide. Centrifuge the Bi_2S_3 precipitate, wash the precipitate with H_2O and discard the supernates. Repeat Step 1 to form BiOCl.
4) Dissolve BiOCl in 10 ml of 2-N HCl. Dilute to 15 ml with H_2O, heat the solution and add 10 mg of Ag carrier. Centrifuge, filter the supernate and reject the AgCl precipitate. Add dilute NH_4OH to the supernate until $Bi(OH)_3$ precipitates. Centrifuge and discard the supernate.
5) Dissolve the $Bi(OH)_3$ in 30 ml of 6-N HCl. Transfer the solution to a separatory funnel and shake with an equal volume of methyl isobutylketone (MIBK, hexone). Reject the organic phase. Add another 30 ml of MIBK and 0.5 g of solid NaI. Extract bismuth iodide into the organic phase, and discard the aqueous phase. Wash the organic phase with 30 ml of 6-N HCl containing 0.5 g NaI. Add 15 ml of 6-N HCl and 0.5 g of solid $NaNO_2$ to the organic phase and swirl. When the reaction has ceased, back-extract Bi into the aqueous phase (the organic phase should be yellow and the aqueous phase colorless). Drain the aqueous layer into a 40-ml centrifuge tube, and add NH_4OH to precipitate $Bi(OH)_3$. Centrifuge and wash the precipitate with H_2O.
6) Dissolve the $Bi(OH)_3$ precipitate in 2 ml of conc. HNO_3 and dilute to 10 ml with H_2O. Add 0.5 g of trisodium phosphate, boil the solution, and dilute to 40 ml with H_2O. Cool and let the bismuth phosphate settle, centrifuge and discard the supernate.
7) Dissolve the precipitate by warming with 2 ml of conc. HCl, dilute, and add 6-N NaOH to precipitate bismuth hydroxide. (This step removes any

Pb as plumbite). Centrifuge and discard the supernate. Dissolve the precipitate in 10 ml of 2-N HCl and transfer to a new centrifuge tube. Add NH_4OH to precipitate $Bi(OH)_3$. Centrifuge and discard the supernate.

8) Dissolve the precipitate in 1 ml of 6-N HCl. Heat, precipitate BiOCl with excess H_2O. Allow to stand, centrifuge and discard the supernate.
9) Make a slurry with H_2O and filter the BiOCl onto a pre-weighed filter paper. Wash the precipitate with H_2O and methanol. Dry in an oven at 110°C for 10 minutes, cool, weigh and mount for counting. Count the ^{210}Bi ($t_{1/2}$ - 5.0 d) beta activity (1.16 MeV) in a low background (0.2-0.5 cpm) beta-proportional counter. Correct the activity for self-absorption (Note 3). Chemical yields range from 60-70 percent.

The irradiated bismuth standard is dissolved in the presence of Bi carrier and diluted to 100 ml in a volumetric flask. A 5-ml aliquot of this solution is pipetted into a centrifuge tube containing 30 mg of Bi carrier. Steps 2 (without hold-back carriers) through 9 are carried out.

Notes:

1) Iridium is the main contaminant in Bi chemistry when meteorite and lunar samples are analyzed.
2) Cerium(IV) keeps iridium in the IV oxidation state, which is adsorbed strongly on the column. Ammonium hexanitratocerate (IV) is used in conditioning the column; and cerium(IV) sulfate is used in eluting Bi with 1-M H_2SO_4.
3) Beta self-absorption correction for ^{210}Bi in BiOCl is generally about 2% per mg cm^{-2} thickness.

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