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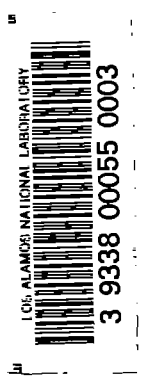
The Radiochemistry of Lead



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The Radiochemistry of Lead

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Issuance Date: August 1961

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

Printed in USA. Price $1.75. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry

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

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

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

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

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This report 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 Academy of Sciences.

This report is intended to contain information primarily of interest to radiochemists. However, the increasing interest of the so-called radiochemist in problems involving mineral, meterological, biological and environmental samples and the continuing use of radiochemical techniques by biologists, biochemists, organic, analytical 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 lead from a few radioelements.

The standard radiochemical procedures for lead are included and form the basis of most of the detailed radiochemical procedures compiled in section VII. In addition, a special attempt has been made to give information on techniques which have demonstrated or promise potential advantages for radiochemical application but are not in general use by radiochemists.

Undoubtedly, important references and procedures have been left out. Notification of such omissions or new techniques for inclusion in future revisions of this manuscript would be much appreciated.

I would like to acknowledge the aid of E. K. Hyde of the Lawrence Radiation Laboratory in Berkeley, who kindly made his extensive file on the radiochemistry of lead available to the author at the beginning of this study and the perserverance and perspicacity of Miss Nancy Hughes, who typed the drafts and final manuscript.

W. M. Gibson

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The Radiochemistry of Lead

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I. General reviews of the inorganic and analytical chemistry of lead.

W. W. Scott (N. H. Furman, Ed.): "Standard Methods of Chemical Analysis", 5th Edition, D. Van Nostrand Co., Inc., New York, 1939.

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

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

II. General reviews of the radiochemistry of lead.

O. Hahn: "Applied Radiochemistry", Cornell University Press, Ithica, New York (1936).

Although not a general review, this book discusses much of the early radiochemistry of lead.

III.

Table I
Table of isotopes of lead.

Isotope	Half life	Type of decay	Method of Production
Pb^{195}	17 m	E.C.	
Pb^{196}	37 m	E.C.	
Pb^{197M}	42 m	E.C. 80%, I.T. 20%	
Pb^{198}	2.4 h	E.C.	
Pb^{199M}	12.2 m	I.T.	
Pb^{199}	90 m	E.C., β^+ weak	
Pb^{200}	21.5 h	E.C.	$Hg^{198}(\alpha,2n)$
Pb^{201M}	61 s	I.T.	
Pb^{201}	9.4 h	E.C., β^+ weak	$Hg^{198}(\alpha,n)$;$Hg^{199}(\alpha,2n)$
Pb^{202M}	3.62 h	I.T. 90%, E.C. 10%	
Pb^{202}	$\sim 3 \times 10^5$ y	E.C.	$Hg^{199}(\alpha,n)$;$Hg^{200}(\alpha,2n)$
Pb^{203M}	6.1 s	I.T.	
Pb^{203}	52.1 h	E.C.	$Hg^{201}(\alpha,2n)$;$Tl^{203}(p,n)$;$Tl^{203}(d,2n)$
Pb^{204M}	66.9 m	I.T.	
Pb^{204}	stable		1.40%
Pb^{205}	$\sim 5 \times 10^7$ y	E.C.(no γ)	
Pb^{206}	stable		25.1%
Pb^{207M}	0.80 s	I.T.	daughter Bi^{207}
Pb^{207}	stable		21.7%
Pb^{208}	stable		52.3%
Pb^{209}	3.30 h	β^-(no γ)	Pb (n,γ) daughter Tl^{210}(RaC")
Pb^{210}(RaD)	19.4 h	β^-	daughter Po^{214}(RaC)
Pb^{211}(AcB)	36.1 m	β^-	daughter Po^{215}(AcA)
Pb^{212}(ThB)	10.64 hr	β^-	daughter Po^{216}(ThA)
Pb^{214}(RaB)	26.8 m	β^-	daughter Po^{218}(RaA)

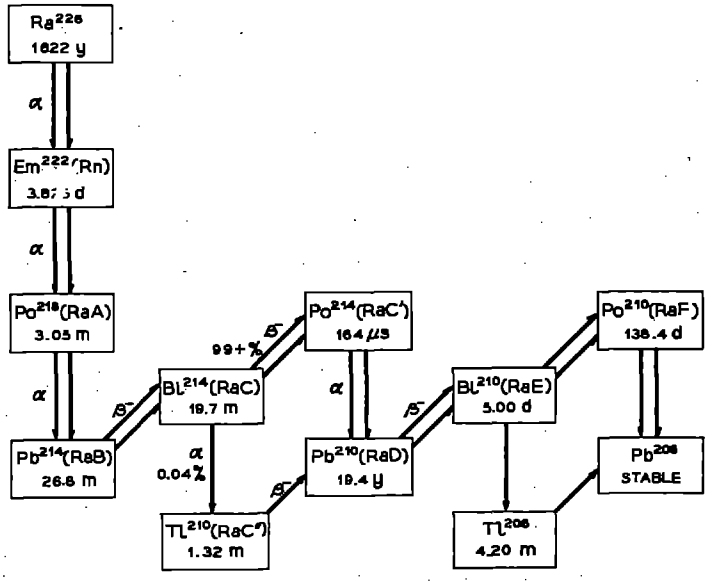
For more complete information on the radiations of the lead isotopes and for references to the original literature, see "Table of Isotopes", D. Strominger, J. M. Hollander and G. T. Seaborg, Reviews of Modern Physics 30, No. 2, part II, April 1958. Lead-210 (RaD), lead-212 (ThB) and lead-214 (RaB) and their daughters have been widely used as tracers and sources. These isotopes are commonly obtained from natural radium and thorium samples. The genetic relationships of the radium and thorium series are shown in Figure 1 and Figure 2.

IV. Review of those features of lead chemistry of chief interest to radiochemists.

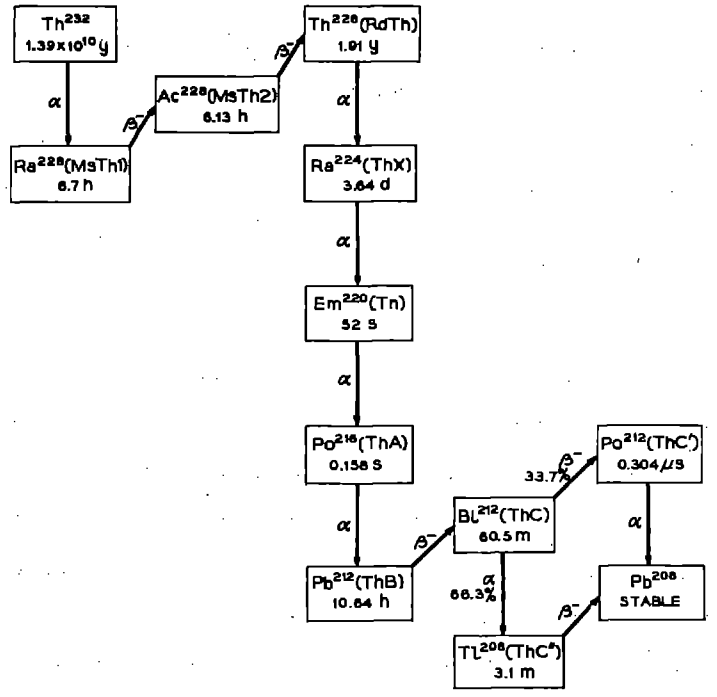
1. General comments.

The radiochemistry of lead has a history almost as long as the history of radiochemistry itself. In 1899, three years after the discovery of radioactivity by Becquerel and only a year after the discovery of radium and polonium by the Curies, Elster and Geital reported that lead sulphate obtained from pitchblend was very active (El). This was interpreted at the time as being due to activity induced in stable lead by exposure to the radiations of radium in the ore and was called "radiolead". The true interpretation for this result and the other experiments that followed it, however, had to await the transmutation hypothesis of Rutherford and Soddy in 1902-1903 but the name "radiolead" was still applicable.

The existence of convenient radioactive isotopes of lead in the natural series brought about their early use as indicators. The first published account of the use of a radioactive tracer was in 1913 when Hevesy and Paneth measured the solubility of lead chromate (H1) by using ThB (Pb^{212}) tracer. It is reported that an emminently practical application was devised by Hevesy even prior to this. The story goes that Hevesy had unconfirmed suspicions about the culinary practices at the boardinghouse at



1. Radium decay series.



2. Thorium decay series.

which he resided during his early work on radioactivity. One evening after a repast of the inevitable "stew", he left a sizable portion of his dinner uneaten after spiking it with a neutral solution of ThB he had prepared for the purpose. The next evening armed with an electroscope and a suitable demonstration source it is said that Hevesy proceeded to show his surprised fellow boarders and embarrassed landlord that the stew was being recycled in a most unforgivable manner. Already by 1926 lead isotopes were in use in an extremely diverse number of fields (H2).

The recent book by Overman and Clark (02) gives a good review of radioisotope techniques. This is especially useful to a worker new in the field as a guide to handling radioisotopes and planning experiments involving radioisotopes.

2. Metallic lead.

Lead metal is a silver gray metal, soft, dense and fusible. In spite of its fairly low melting point of 328°C it is often used as a target for cyclotron irradiations at moderate current densities. Some care must be taken to provide adequate cooling, however, since the thermal conductivity (0.082 at 100°) is only moderate.

The physical properties of lead are tabulated in Table II. Although lead is rarer than the so-called "rare metals" (abundance 1.6×10^{-3}% in earth's crust) its frequent occurrence in sizable deposits, the ease of obtaining the metal and the widespread use of lead in alloys, paints, fuels, pipes and other materials make it a frequent contaminant of reagents, air, dust and laboratory glassware and materials. The problems of preparing carrier-free samples are discussed in a later section of this report.

Table II
Physical and atomic properties of lead.

Atomic Wt.	207.22
Atomic No.	82
Stable Isotopes	204(1.40%), 206(25.1%), 207(21.7%) 208(52.3%)
Melting Point, °C	327.5
Boiling Point, °C	1750
Density, g/cc	11.34
Electrical resistivity, ohm-cm at 20°C	21.9×10^{-6}
Size of M^{+4} in Crystal, cm x 10^{8}	0.84
Ionization Potentials	
1st electron	7.38
2nd electron	14.96

It is of interest for many radiochemical applications that the isotopic abundances in a particular lead sample are somewhat dependent on its history. Lead derived from uranium ores is principally Pb^{206} and its density is 11.27 as opposed to 11.34 for ordinary lead which contains more lead-208 than any other isotope (abundances are shown in Table I).

Lead is easily reduced to the metal and is usually separated from its most common ore galena (PbS) by heating with scrap iron which reduces the lead. The reduction is of interest in a number of useful separation schemes which are discussed in section IV-10 of this report. The oxidation potentials (L1) in acidic and basic systems are shown below.

Acid solution $\quad Pb \xrightarrow{0.126} Pb^{++} \xrightarrow{-1.455} PbO_2$

Basic solution $\quad Pb \xrightarrow{0.54} PbO \xrightarrow{-0.28} PbO_2$

Lead can be dissolved easily in dilute nitric acid, but is quite resistant to the action of even moderately concentrated sulfuric acid. The metal can be dissolved in concentrated sulfuric acid and is readily oxidized by oxygen in the presence of weak organic acid such as acetic acid.

3. Soluble salts of lead.

The salts of lead easily soluble in water include the nitrite, nitrate, chlorate, bromate, perchlorate, dithionate, citrate and acetate salts. Although the dihalides $PbCl_2$, $PbBr_2$ and PbI_2 are only slightly soluble in cold H_2O their solubility is increased in concentrated halogen acids due to formation of complex ions (e.g. $PbCl_4^=$). Lead hydroxide is only slightly soluble in water but is soluble in acid or alkaline solutions. In basic solutions basic nitrates are formed which precipitate; however, in the presence of excess acetate, basic lead acetate $Pb(OH)C_2H_3O_2$ is formed which is soluble in basic solution and can be used to prevent precipitation or hydrolysis of lead in neutral or weakly basic solutions.

The only oxidation state of importance in aqueous solution is the +2 state. Compounds of the +4 plumbic ion are well known but are invariably unstable or insoluble in aqueous solution. Due to the dominant stability of the +2 state in aqueous solution oxidation-reduction reactions are of minor importance in lead separations and determinations. The notable exceptions are anodic oxidation to the dioxide and reduction to the metal either cathodically or by internal electrodeposition. These reactions have been used for the separation and determination of lead and are discussed in detail in section IV-10 of this report.

The information available (H4), (L5) and (S4) on the solubility of the common soluble lead compounds is shown in Table III.

4. Insoluble salts of lead.

A. Insoluble salts and gravimetric compounds.

The common insoluble salts of lead are summarized in Table IV. Some of these salts as well as some of the other lead salts and organic complex precipitates are discussed below.

Table III
Soluble salts of lead.

Compound	Formula	Solubility in Water* g/100 ml
Acetate	$Pb(C_2H_3O_2)_2 \cdot 2H_2O$	45.61^{15}, 200^{100}
Bromate	$Pb(BrO_3)_2$	1.38^{20}
Chlorate	$Pb(ClO_3)_2$	151.3^{18}, 171^{80}
perChlorate	$Pb(ClO_4)_2$	499.7^{25}
Nitrate	$Pb(NO_3)_2$	37.65^{0}, 56.5^{20}, 127^{100}
Dithionate	$Pb\ S_2O_6$	$115.0^{20.5}$

*At temperature in degrees centigrade shown in superscript

TABLE IV
Insoluble Salts of Lead

Name	Formula	Solubility in Water* (g/100ml H_2O)	Solubility in Other Solvents**
Bromide	$PbBr_2$	0.4554^{0}, 0.844^{20}, 4.71^{100}	s. a., KBr; sl. s. NH_3; i. al.
Carbonate	$PbCO_3$	0.00011^{20}	s. a., alk.; i. al, NH_3
Chloride	$PbCl_2$	0.673^{0}, 0.99^{20}, 3.34^{100}	sl. s. dil. HCl, NH_3; i. al.
Chromate	$PbCrO_4$	$5.8 \times 10^{-6(20)}$	s. a., alk.; i, ac. a., NH_3
diChromate	$PbCr_2O_7$	d.	s. a., alk.
Ferrocyanide	$Pb_2Fe(CN)_6 \cdot XH_2O$	i.	sl. s. H_2SO_4
Fluoride	PbF_2	0.064^{20}	s. HNO_3; i. acet., NH_3
Hydroxide	$Pb(OH)_2$	0.0155^{20}, sl. s.^{100}	s. a. alk.; i. acet.
Iodate	$Pb(IO_3)_2$	0.0012^{2}, 0.003^{25}	sl. s. HNO_3; i. acet.
Iodide	PbI_2	0.044^{0}, 0.063^{20}, 0.41^{100}	s. alk., KI; i. al.
Laurate	$Pb(C_{12}H_{23}O_2)_2$	0.009^{35}	
Molybdate	$PbMoO_4$	i.	d. conc. H_2SO_4; s. a., KOH; i. al.
Oxalate	PbC_2O_4	0.00016^{18}	s. HNO_3; i. alk.
Oxide	PbO	0.0017^{20}	s. HNO_3, alk., lead acet., NH_4Cl, $SrCl_2$
diOxide	PbO_2	i.	s. dil. HCl; sl. s. ac. a.
Orthophosphate	$Pb_3(PO_4)_2$	0.000014^{20}	s. HNO_3, alk.; i. ac. a.
Selenate	$PbSeO^4$	i.	s. conc. a.
Sulfate	$PbSO_4$	0.00425^{25}, 0.0056^{40}	s. NH_4 salts; sl. s. conc. H_2SO_4
Sulfide	PbS	0.000086	s. a.; i. KOH, al.
Thiocyanate	$Pb(SCN)_2$	0.05^{20}	s. KCNS, HNO_3
Thiosulfate	PbS_2O_3	0.03	s. a. $Na_2S_2O_3$
Tungstate	$PbWO_4$	0.03	d. a.; i. al.

*At temperature in degrees centigrade shown in superscript.
**Abbreviations used in the "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co. have been adopted

Lead carbonate

Lead carbonate is slightly soluble in water, is insoluble in basic solution and is soluble in ammonium acetate and in acid solution. The carbonate is frequently formed during separations by metathesizing a lead sulphate precipitate to lead carbonate through heating and stirring the lead sulfate with portions of sodium carbonate solution.

Lead carbonate can be precipitated homogeneously by addition of monoethanolamine carbonate reagent to a neutral nitrate solution. The monoethanolamine carbonate reagent is prepared by saturating a 10% monoethanolamine solution with carbon dioxide gas and adding an equal amount of 10% monoethanolamine. This reagent has been used to separate lead from copper by addition of a 1.5% solution of the reagent to a neutral solution of lead and copper nitrates (R2). The lead carbonate precipitate was washed with water containing a small amount of the carbonate reagent and subsequently dissolved in a hot nitric acid, acetic acid mixture. After neutralization the precipitation can be repeated. The specificity of this precipitation, especially in the presence of acetate, tartarate or cyanide would seem to be worthy of further investigation.

Lead Chloride

Lead chloride precipitation is not quantitative for lead under normal conditions but can be useful for radiochemical purification of a lead fraction. It can also be used to remove the bulk of a large quantity of lead prior to more complete separations. Although sparingly soluble in cold water, lead chloride ($PbCl_2$) is readily soluble in hot water or in dilute, hot nitric acid. This has been used as a separation from silver by precipitation of silver chloride from hot nitric acid solutions (H3). Tira (T1) reports that the condition for maximum yield of $PbCl_2$ with hydrochloric acid at 20°C occurs at pH 0.5

in lead chloride solution and pH 0.03 in lead acetate solution. Increasing the chloride concentration too high results in formation of soluble lead chloride complexes such as $PbCl_4^=$.

An excess of ethylenediaminetetraacetic acid (EDTA) causes lead to be soluble in chloride solutions (Cl) due to formation of the very stable EDTA-lead complex. Silver (I) and thallium (I) chlorides remain insoluble and can be separated from lead. Mercury (I) also forms a soluble EDTA complex under these conditions. The presence of citrate also keeps lead from precipitating from dilute chloride solutions. Mukherji and Dey have used this to separate lead from silver (M4). In their procedure an excess of sodium citrate is added to the mixture containing silver and lead nitrate. The insoluble citrates of lead and silver which are at first precipitated redissolve upon gentle heating as complex citrates. Upon addition of dilute hydrochloric acid silver chloride precipitates. Lead may be removed from the filtrate as lead chromate.

Other Lead Halides

Lead bromide and lead iodide are sometimes used for analytical separations. The dibromide is slightly soluble in cold water and readily soluble in hot. The diiodide is only slightly soluble in cold or hot water. In the presence of EDTA in acid solution lead and Bi are not precipitated as the iodide whereas silver (I) and thallium (I) remain insoluble (Cl).

Lead Chromate

Along with the sulfide and sulphate, precipitation of lead chromate is one of the most popular separations in lead radiochemistry. This precipitation serves as a satisfactory separation from copper, zinc and other elements that form soluble chromates in acetic acid solution. Thallium, antimony, bismuth and barium are precipitated or carried with the lead chromate; however, bismuth contamination can be reduced by leaching the

precipitate with a dilute citrate-acetate solution (H3).

Moore reports that from a mixture of lead and bismuth chromates all the bismuth chromate and up to 20% of the lead chromate is dissolved by citric acid solution (M5). He reports similar results if the chromates are precipitated from a citric acid solution.

Addition of EDTA to the acetic acid solution causes lead (and silver) to remain in solution upon addition of chromate. Thallium and barium precipitate (C1).

Lead Hydroxide

Except in the presence of fairly large amounts of aluminum or iron (III), lead is incompletely precipitated as the hydroxide from ammonium hydroxide solutions. The hydroxide is amphoteric, going into solution in strong alkaline solutions due to formation of plumbite, $HPbO_2^-$, ions. In the presence of EDTA, lead is even less inclined to precipitate as the hydroxide or to be carried on hydroxide precipitates. Precipitation of bismuth hydroxide from a 0.1 N NaOH solution containing excess EDTA has been used as a separation of lead and bismuth (L3). The lead was subsequently removed from the filtrate by precipitation of the bismuthiol I (2,5-dimercapto-1,3,4 thiodiazol) complex. This procedure was reported to give > 90% yield of pure lead and bismuth in less than 15 minutes (L3).

Lead Molybdate

Precipitation of lead molybdate is a desirable method for lead separation in the absence of alkaline earths that form insoluble molybdates and of substances such as titanium, tin and bismuth that are easily hydrolyzed. This is sometimes used as a separation from barium (H3).

Lead Nitrate

Although lead nitrate is usually regarded as one of

the soluble salts of lead it can be precipitated from cold solutions by addition of fuming nitric acid. This has been used as a separation from bismuth (R1), (N1).

Lead Dioxide

Precipitation of lead dioxide by anodic deposition on a platinum gauze electrode is a standard method of separation and determination for lead (H3). In the standard procedure the presence of chloride ion, mercury, arsenic, tellurium, selenium and phosphorus prevent the complete deposition of lead, while bismuth, tin, antimony, and manganese co-deposit. The use of controlled potential deposition and complexing agents make this separation method much more selective (L4). The electroanalytical method has been important for lead analysis and is discussed in detail in section IV-10.

Lead Sulfate

The most common separation of lead by radiochemists is that based on the insolubility of its sulfate. This is also the outstanding separation method in the classicla analysis of lead (H3). For complete precipitation it is necessary to remove traces of nitrate and chloride ions by evaporating to SO_3 fumes several times. The sulfate is insoluble in dilute sulfuric acid but is soluble in concentrated sulfuric acid especially with heating.

Silica, if present, separates with the lead sulfate as does tungsten, niobium, tantalum, barium and less completely strontium and calcium. Bismuth, antimony and silver contaminate the lead to some extent. The coprecipitation of antimony is decreased by addition of tartaric acid. Addition of alcohol to the sulfate solution decreases the solubility of lead sulfate but increases contamination by silver, bismuth or calcium. The normal separation based on the sulfate involves dissolution of the lead sulfate in ammonium acetate solution. Hydroxide

insoluble materials such as silica, or bismuth are not dissolved and are removed by filtration or centrifugation. Barium sulfate is slightly soluble in ammonium acetate and also tends to prevent complete dissolution of lead sulfate. If large amounts of barium are present a barium-lead separation (such as precipitation of lead sulfide) should be carried out prior to the sulfate precipitation.

The lead sulfate precipitate can be made somewhat more crystalline and more easily filtered and washed by homogeneous precipitation through addition of dimethyl sulfate. The procedure recommended by Elving and Zook involves precipitation of lead sulfate from a solution of 70% methyl alcohol, 28% dilute nitrate solution and 2% dimethylsulfate (E2). This mixture is digested one hour at 90° with occasional addition of a 70% methanol solution to keep the volume about 100 ml. After cooling in ice the precipitate is then filtered. It was reported (E2) that good separation is achieved from nickel, manganese, copper and zinc but that large amounts of aluminum and iron prevent quantitative precipitation of lead.

The EDTA complex of lead is sufficiently stable to prevent lead sulfate from precipitating under certain conditions. For example, radium sulfate can be separated from RaD(Pb^{210}) by addition of ammonium sulfate to a weakly acid (pH 4.5-5) solution containing EDTA (V1).

Lead Sulfide

Lead sulfide is the most insoluble of the simple lead salts, having a solubility product constant of 3.4×10^{-28}. Precipitation of lead sulfide from nitric acid solution is very nonselective, carrying not only members of the copper group and arsenic group but also thallium, indium and gallium as well as some vanadium or tungsten in the absence of tartaric acid (H3).

Alkaline lead sulfide is somewhat more selective but

still carries a host of elements. The principal contaminants are the other members of the copper group, silver, mercury, bismuth and cadmium as well as ruthenium, rhodium and palladium. It is better to separate members of the arsenic group by precipitating the sulfides from alkaline solution by addition of ammonium sulfide than by leaching an acid sulfide precipitate with alkaline solution. The presence of tartarate during the alkaline sulfide precipitation prevents precipitation of a number of elements which would otherwise separate as hydroxides, while cyanide inhibits precipitation of silver or copper (H3). Lead sulfide is soluble in concentrated hydrochloric acid and in hot 2N nitric acid.

Moore (M5) reports that excellent separation of traces of lead from small amounts of bismuth can be achieved by: adding 0.02 grams of copper to 25 ml of the lead and bismuth in 2N hydrochloric acid and saturating the solution with hydrogen sulfide gas. The copper sulfide precipitate was then filtered and washed with 2N hydrochloric acid saturated with hydrogen sulfide. The lead was recovered from the filtrate and bismuth from the precipitate. The lead presumably was kept from precipitation because of formation of soluble lead chloride complexes.

Precipitation of lead sulfide homogeneously by addition of thioacetamide has been reviewed by Finston and Miskel (F2). The precipitate forms slowly in neutral or dilute acid solutions (up to 0.1 N hydrochloric or 0.3 N nitric acid). The precipitate forms rapidly from an acid solution made ammoniacal. The advantage of the homogeneous precipitation is the production of a coarse, crystalline, easily filtered precipitate and reduction of occluded contaminants (F2). Separations using thioacetamide can be made more specific by the addition of EDTA (F3). Some cations such as cadmium, cobalt, iron and nickel fail to precipitate from ammoniacal solution due to formation of EDTA complexes. The precipitation of lead is delayed. In the presence

of tartarate and EDTA in ammoniacal solution tin sulfide does not precipitate.

Salaria has described a number of separations based on the use of sodium sulfide (S1), (S2) and (S3). Binary separations of lead from platinum, gold, selenium, arsenic, rhenium, molybdenum, tellurium, antimony and alkaline earths are described. In most of these separations lead sulfide is precipitated from a neutral solution containing excess ammonium acetate following the removal of the other metal sulfide from hot 6N hydrochloric acid solution by addition of the Na_2S reagent (prepared by passing hydrogen sulfide gas into sodium hydroxide solution at less than 5°C). The separations described give good lead yields but the completeness of the separation should probably be checked before application to radiochemical procedures. More convenient separations exist for most of these mixtures.

Precipitation on Ion Exchange Columns

Separation of lead from other members of the silver group or copper group has been achieved by Komlev and Tsimbalista (K2) by precipitation on a column packed with either Al_2O_3 or synthetic resin well ground with the precipitant. The ions to be separated were either poured onto a 3-4 mm diameter column packed with 4-5 cm of the dry charge or in some cases it was found beneficial to moisten the packed column mixture with a solution of the precipitant before use.

For separation of silver, lead and mercury a moist column of Al_2O_3 and potassium iodide was used. Separate zones of AgI, Hg_2I_2 and PbI_2 appeared. With the copper group (Cu, Cd, Pb, Bi), Al_2O_3 moistened with saturated Na_2S or 2N $(NH_4)_2S$ solution was used (K2).

Lead 8-hydroxyquinoline (lead oxine)

This reagent has been used frequently in the analytical chemistry of lead but the measurable solubility of the lead com-

plex has caused its use to be questioned (F4). For radiochemical separations where quantitative recovery is not required this is not a strong objection and the pH dependence of precipitate formation for many ions makes this a useful reagent. Table V taken from data in reference F4 shows the pH range for complete precipitation for a variety of ions. Due to the high pH required to precipitate lead a number of separations appear possible. For example, bismuth, cadmium, cobalt, copper, iron III, manganese, and zinc could be removed from acid solution with the lead precipitating after addition of sodium hydroxide. Lead precipitates as $Pb(C_9H_6ON)_2$. The selectivity of the 8-hydroxyquinoline precipitation can be apparently increased by the use of EDTA as a masking agent although only a few selected pH values have been investigated (see ref. C1, p. 210).

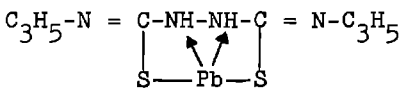
Table V
pH range for complete precipitation of metal 8-Hydroxyquinolates*.

Metal	pH
Aluminum	4.2 to 9.8
Bismuth	4.8 to 10.5
Cadmium	5.4 to 14.5
Calcium	9.2 and higher
Cobalt	4.2 and higher
Copper (II)	5.3 and higher
Iron (III)	2.8 to 11.2
Lead	8.2 to 12.3
Magnesium	8.2 and higher
Manganese (II)	5.9 to 10
Molybdenum (VI)	3.3 to 7.6
Nickel	4.3 and higher
Thorium (IV)	4.4 to 8.8
Titanium (III)	4.8 to 8.6
Tungsten (VI)	4.9 to 5.7
Uranium (VI)	4.1 to 8.8
Vanadium (V)	2.7 to 6.1
Zinc	4.4 and higher

*Data from J. F. Flagg, "Organic Reagents Used in Gravimetric and Volumetric Analysis", Interscience Publishers, New York (1948).

Lead Diallyldithiocarbamido-hydrazine

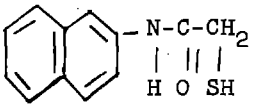
Lead has been found to precipitate quantitatively with diallyldithiocarbamidohydrazine between pH 5 and 6 (D2). The complex has the form:



Because of the pH dependence of the precipitation some useful separations are possible. Lead and copper have been separated (D2) by first precipitating the copper complex from dilute acid solution, then raising the pH with sodium hydroxide to the point where the lead complex is precipitated.

Lead Thionalide

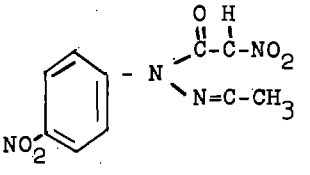
This reagent can be used for precipitation of most of the elements which normally precipitate from acid solution with hydrogen sulfide (F4). The form of the organic molecule is:



This reagent can be made somewhat more selective than the normal hydrogen sulfide treatment since many members of the "sulfide insoluble" group can be prevented from precipitating by addition of suitable masking agents. By precipitation from alkaline solution containing tartarate and cyanide, lead can be separated from aluminum, arsenic, cadmium, chromium (IV), cobalt, iron (III), nickel, silver, titanium (IV), and zinc (F4). The presence of sulfate ions (> 1%) or chloride ions (> 4%) results in incomplete lead precipitation.

Lead Picrolonate

Lead is precipitated by picrolonic acid (1-p-nitrophenyl-3-methyl-4-nitropyrazol-5-one) from neutral or weakly acid solutions (pH range 2-6.5) as a crystalline salt, $Pb(C_{10}H_7N_4O_5)_2 \cdot 1{,}5\ H_2O$ (F4). The structure of the organic molecule is:



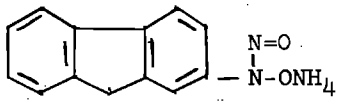
This reagent is very sensitive for lead and can be used to separate and determine microgram quantities. Lead can be separated from aluminum, antimony, arsenic, barium, bismuth, cadmium, chromium, cobalt, copper, iron (III), magnesium, mercury, nickel, silver and zinc using the following procedure (F4): to a 1 to 2 N nitric acid solution of the metal add an equal volume of saturated thiourea in 1 N nitric acid. Upon cooling to ice temperature a precipitate of 2 $Pb(NO_3)_2 \cdot 11CS(NH_2)_2$ separates. This precipitate is filtered and washed with cold 1 N nitric acid saturated with thourea. The precipitate is dissolved in hot water and 0.1 M picrolonic acid is added slowly to the boiling solution. After digestion the solution is cooled, and the precipitate is washed with cold water, dried at 130°-140°C and weighed. The precipitate contains 27.25% lead. Thallium interferes.

Lead Mercaptobenzothiozole

Separation and determination of lead in the presence of up to 100 times as much barium with mercaptobenzothiazole has been reported (R3). It was found that separation from barium could be achieved best from an ammonium hydroxide-ammonium nitrate buffer solution. The temperature of the solution and the dilution was found to have little influence on the results (K3).

Other Organic Precipitants

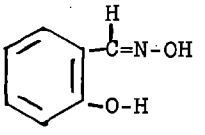
A 2-fluorenyl anolog of cupferron with the structure



which forms a white precipitate with lead from neutral solution has been reported (O1).

At pH 8.9 or higher, lead is precipitated as $PbC_1H_5O_2N$ by salicylaldoxime (F4). The structure of the reagent

is:



Use of a strongly ammoniacal solution permits separation from silver, cadmium and zinc (F4).

Bismuthiol I (2,5-dimercapto-1,3,4-thiodiazol) has been used to precipitate lead from a 0.1 N sodium hydroxide solution containing excess EDTA (L3). This has been used to separate lead from bismuth (L3).

Lead can be precipitated from cold, nearly neutral solution by anthranilic acid (F4). This is not a very selective separation.

B. Coprecipitation of lead.

The coprecipitation behavior of lead has been studied more thoroughly and systematically than almost any other element. This stems principally from the availability of carrier-free ThB (Pb^{212}) from thorium ores and its convenient half-life and decay characteristics which lead to its widespread use in the study of the chemical behavior of unweighable amounts of radioactive species. Most of these studies were carried out in the period between 1905 and 1930 and are summarized by Hahn (H5). These studies led to the "precipitation rule" of Fajens, the "Fajens-Paneth precipitation and absorption rule" and finally to Hahn's "precipitation and absorption law" sometimes referred to as the "Fajens-Paneth-Hahn Law". These studies which are essential to the understanding and manipulation of any carrier-free material in aqueous solution indicated that in cases where the tracer material forms a mixed crystal with the carrier precipitate then the lower the solubility of the compound formed by the radioelement with the anion of the precipitant, the greater the amount of the radioelement carried down as cation.

In this case the separation is practically independent of the conditions of precipitation. On the other hand, if the process is an adsorption phenomena, then the separation depends markedly upon the conditions of precipitation. Both of these cases are, of course, strongly affected by the presence of complexing species in the solution. Most of the material in this section is taken from Hahn's book (H5) although a few more recent observations are included.

The importance of formation of mixed crystals in coprecipitation phenomena and its application to separations is illustrated by the behavior of carrier-free lead in the presence of barium or radium halides. Both $PbCl_2$ and $PbBr_2$ crystallize as the anhydrous salt in the rhombic system as does $BaCl_2$ and $RaCl_2$. On the other hand $BaBr_2$ and $RaBr_2$ crystallize in the monoclinic system. Lead tracer is carried by barium chloride (W4) and radium chloride (H5) but is not carried by barium bromide (W4) or radium bromide (H5) precipitates from strong hydrobromic acid solutions in spite of the low solubility of lead bromide. This behavior has been used to separate tracer lead from radium salts (H5, p. 102).

The remainder of this section is separated into three parts. The first part treats those cases where the coprecipitation of lead is either quantitative or relatively nonvariable under a variety of precipitation conditions (called precipitation). Most of these cases involve the formation of mixed crystals. The second part treats examples of cases where the amount of coprecipitation is sensitive to the conditions of precipitation (called adsorption) and part three considers the effect of adding complexing agents to the solution (called complexing action).

1. Precipitation

The behavior of lead with precipitates with which it forms mixed crystals is illustrated by its coprecipitation with

alkali halides. Although this system is not of particular importance for separations the constancy of the partition coefficient under a variety of conditions is illustrative of this general class. The potassium chloride system is shown in Table VI. The partition coefficient is defined as the ratio of ThB(Pb^{212})/potassium in the crystals compared with the ratio ThB/potassium in the solution. Similar results were obtained with sodium chloride, and potassium bromide for which the partition coefficient was about 60 (H5, p. 104). In these experiments the amount of lead was varied from the most carrier-free ThB available ($< 10^{-10}$ M) up to several mol per cent of lead.

Other salts of somewhat more interest to the radiochemist which exhibit the same type of behavior are: barium carbonate, barium sulfate, radium sulfate, radium chloride, radium sulfate (H5), lanthanum carbonate, barium chloride, silver chromate (W4) and barium nitrate (H6). Mercury (II) sulfide, although not studied in sufficient detail to warrant classification is reported to carry lead under a variety of conditions (I2). Coprecipitation of lead with mercury (II) sulfide is especially useful since the mercury can be removed subsequently by sublimation. This is accomplished by dissolving the mixed lead and mercury sulfides in aqua regia, evaporating the solution to dryness, adding excess powdered sulfur and igniting the mixture. The mercuric sulfide sublimates leaving a precipitate of lead sulfide which can be dissolved in nitric acid by dropwise addition of hydrogen peroxide (I2).

Although probably not similar in the sense of isomorphous inclusion of lead, iron (III) hydroxide and aluminum hydroxide carry lead so effectively from ammonium solution under such a variety of conditions that we include them here. Lead has been quantitatively concentrated in large rain-water samples by adding app. 0.2 grams of aluminum sulfate per gallon of water,

Table VI
Coprecipitation of thorium B(Pb^{212}) from supersaturated solutions of potassium chloride at 0°C.*

Per cent in the Precipitate		Partition coefficient**
KCl	Pb^{212}(ThB)	D
6.4	81.1	57.8
7.3	82	58
10.35	86.7	56.2
14.4	90.5	56.8
18.4	92.8	
	Mean	57

* Taken from Table XVIII, p. 103 of ref. H5.
** Defined as the ratio Pb^{212}/K in the precipitate divided by Pb^{212}/K in the solution.

adjusting the pH to pH 7.0 ± 0.1 and allowing the aluminum hydroxide floc to settle overnight (K11).

2. Adsorption

In this section some of the available data showing the effect of changing the precipitation conditions on the coprecipitation behavior of lead are reviewed. As will be seen the fraction of the lead coprecipitated can vary from greater than 90% to less than 1% merely by changing the conditions. This variability can be a nuisance to the radiochemist, producing erratic and seemingly irreproducible yields or it can be useful in performing separations.

Table VII shows the adsorption of Pb^{212}(ThB) on rapidly formed precipitates of calcium sulfate in the presence of alcohol. Table VIII shows the adsorption of Pb^{212} on silver iodide precipitates.

Effects similar to those shown in Tables VII and VIII are observed for the adsorption of lead upon preformed precipitates as indicated by ThB adsorption upon preformed silver iodide (Table IX) and silver oxalate (Table X). Similar results were observed for lead adsorption upon silver phosphate, silver bromide, silver iodate, silver sulfide, and mercurous bromide (H5). The presence of excess

Table VII

Coprecipitation of Pb^{212}(ThB) on rapidly formed precipitates of $CaSO_4$ (gypsum) in the presence of alcohol.*

Precipitant	Precipitated	Adsorbed
5% excess of H_2SO_4	91.4% of gypsum	88.0% of ThB
10% excess of H_2SO_4	93	85.6
10% excess of H_2SO_4	100	92.2
10 fold excess of H_2SO_4	100	98.4
10% excess of $CaCl_2$	85.4	5.2
7 fold excess of $CaCl_2$	100	1.7

*Taken from Table XVI p. 93 of ref. H5.

Table VIII

Adsorption of ThB(Pb^{212}) on silver iodide precipitated from dilute nitric acid (~.004N)solution.*

Precipitant	Adsorbed
5% excess KI	73.1% ThB
10% excess KI	76.9
50% excess KI	72.5
10% excess $AgNO_3$	4.5
50% excess $AgNO_3$	3.6
100% excess $AgNO_3$	2.0

*Taken from p. 93 of ref. H5.

Table IX

Adsorption of ThB(Pb^{212}) upon 0.200 gm of preformed silver iodide from 0.004 N nitric acid.*

Excess KI, millimoles per liter	ThB adsorbed, per cent
0.00	2.1
0.05	43.9
0.15	52.9
0.25	57.9
0.80	67.2
1.2	75.2
2.4	78.6
16.0	84.8

*From Table XXX p. 140, ref. H5.

Table X
Adsorption of Thorium B upon preformed silver oxalate precipitates in 25 cc of 0.004 N nitric acid.*

$Ag_2C_2O_4$ grams	Excess $AgNO_3$ millimoles per liter	ThB adsorbed per cent
0.05	0.0	81.1
0.10	0.0	91.1
0.20	0.0	96.2
0.20	4.0	91.3
0.20	12.0	69.5
0.20	16.0	60.9
0.20	32.0	36.3
0.20	52.0	11.1
0.20	80.0	0.8

*From Table XLI p. 147, ref. H5.

nitric acid can markedly decrease the amount of adsorption. For example ThB adsorbs with 97% efficiency on preformed silver bromide precipitates from solutions containing 0.06 excess potassium bromide with no excess nitric acid. The per cent adsorbed is reduced to 40% in 0.4 N nitric acid and to 14% in 1N nitric acid (H5). On mercurous bromide precipitates in a 0.05 N excess of potassium bromide and no excess nitric acid 12% of the ThB is adsorbed. In 0.01 N nitric acid the adsorption decreases to 1.5%, is 0.5% in 0.10 N acid and is negligible in 0.5 N nitric acid (H5). Hyde and Raby report that precipitation of MnO_2 by addition of potassium permanganate to a RaD,E,F tracer solution to which manganese (II) has been added will carry 47% of the RaD(Pb^{210}) with no excess nitric acid present and 7% from a 4N nitric acid solution.

In addition to the conditions of precipitation, the rate of formation of the precipitate can play an important role. This effect for the adsorption of ThB on silver oxalate and silver sulfate precipitates is shown in Table XI. The use of homogeneous precipitants such as dimethyl sulfate (E2) or thioacetamide (F2) can be of value in controlling the precipitation rate.

Table XI
Separation by adsorption upon rapidly precipitated and slowly crystallized crystals.*

System	Experimental Conditions	Acid Concentration	Separating Ratio (a)
Ag-Pb(ThB) oxalate	rapid, excess of $C_2O_4^=$ ions	0.5 N HNO_3	0.66
	rapid, excess of Ag^+ ions		0.12
	slow crystallization		<0.1
Ag-Pb(ThB) sulfate	rapid, excess of $SO_4^=$ ions	0.02 N H_2SO_4	0.96
	rapid, excess of Ag^+ ions		0.62
	slow crystallization	1N HNO_3	<0.01

*From Table XVII p. 96, ref. H5.

(a) The ratio of the percentage precipitation of the ThB(Pb^{212}) to the percentage precipitation of the macroscopic component.

Table XII
Examples of precipitates which do not coprecipitate lead in spite of low solubility of analagous lead compound.

Precipitate and Conditions	Amount of Lead Adsorbed or Partition Coefficient*
(a) Precipitation of HgI_2	
From hot HCl solution into excess water	0% ThB(Pb^{212})
From alcoholic solution into water	0% ThB(Pb^{212})
(b) Precipitation of Hg_2Cl_2	
From mercurous nitrate and HCl, heated	0% ThB
From mercurous nitrate and NaCl, heated	0% ThB
(c) Precipitation of copper fumerate	
From ammonium fumerate with excess $Cu(NO_3)_2$	0.2% ThB
From $Cu(NO_3)_2$ with excess ammonium fumerate	2.9% ThB
(d) Precipitation of ammonium halides at 20°C	
NH_4Cl	D = 0.08
NH_4Br	D = 0.04
NH_4I (at -20°C)	D = 0.1
(e) Precipitation of RaBr or BaBr from concentrated HBr solution	no adsorption

* The partition coefficient D is defined as the ratio of tracer lead to macroscopic component in the precipitate divided by the ratio of tracer lead to macroscopic component in the solution.

From the standpoint of achieving useful separations the precipitates which do not carry lead are of almost as much interest as those that do. A few precipitates of interest in this regard are summarized in Table XII. In all of these cases the lead is not carried in spite of the low solubility of the analogous lead compounds.

3. Complexing action

Formation of soluble lead complexes reduces the amount of lead coprecipitated in both of the classes considered above. The effect of addition of chloride ion upon the amount of ThB(Pb^{212}) carried on strontium sulfate precipitates are shown in Table XIII. The coprecipitation of ThB on potassium chloride

Table XIII

Adsorption of ThB(Pb^{212}) on strontium sulfate precipitates in the presence of chloride ions.*

KCl in Solution	Per Cent Contained in Precipitate $SrSO_4$	ThB
0	50	99
0.1 N	50	99
1.0 N	50	82
2.5 N	50	30
3.4 N	50	5 to 10

* From Table XIX p. 105 of ref. H5.

solutions of increasing alkalinity is shown in Table XIV. In this case the adsorption of lead decreases as the alkalinity increases because of the formation of the soluble lead plumbite complex. The stable lead ethylenediametetraacetic acid (EDTA) complex has been used to prevent coprecipitation of lead on silver or thallium chloride (C1), silver and thallium iodides (C1), thallium and barium chromate (C1), bismuth hydroxide (L3), radium sulfate (V1) and tungsten, molybdenum, copper (II), iron (III), aluminum, uranium, magnesium or antimony (III), 8-hydroxyquinolate (C1).

Table XIV

Precipitation of ThB(Pb^{212}) by potassium chloride from solutions increasing in alkalinity.

	Per Cent in Precipitate		
KOH in solution	KCl	ThB	D
0	13	90.3	62
0.001 N	12.8	81.3	30
0.01 N	27.8	53.3	3
0.1 N	26.1	1.65	0.6
1.0 N	37	0.45	0.01

C. Pyrolysis

The standard radiochemical separation procedures for lead usually end by precipitation of lead sulfate or lead chromate in which form they are weighed to determine the chemical yield and mounted in a suitable form for measurememt of their radioactivity.

Lead sulfate, the most commonly used compound for yield determinations, can be precipitated from nitric acid solution and is devoid of impurities at temperatures above 271°C (D3). The composition remains stable up to 959°C. Some people prefer to use lead chromate as a final precipitate due to the high drying temperature needed for the sulfate. Lead chromate also has a very long range of stability, from 91°C to 904°C (ref. D3, p. 184). The precipitate is usually dried at 110-120°C. Because of their simplicity the pyrolysis curves for lead sulfate and lead chromate are not reproduced. A number of other suitable lead compounds are sufficiently stable to permit their use for gravimetric determination. The pyrolysis curves of Duval (D3) for a number of lead compounds are illustrated in Figures 3, 4, 5 and 6. The compounds and recommended drying temperatures are summarized in Table XV. The recommended compounds are marked with an asterisk. Compounds not recommended for gravimetric determination and not shown in Table XV are: lead tungstate, lead cyanide, lead vanadate, lead molybdate, lead iodide and lead chlorite (D3).

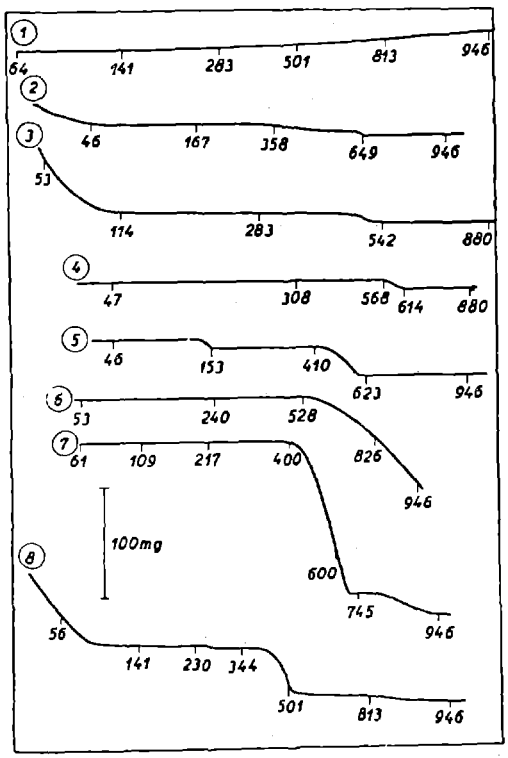


Figure 3

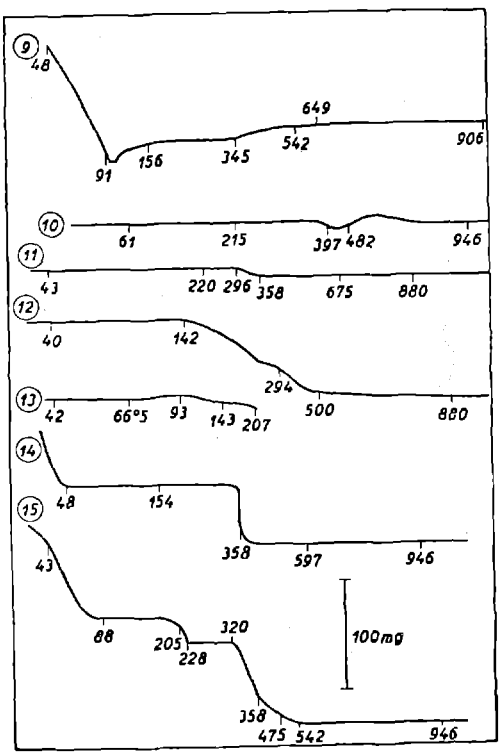


Figure 4

3. Pyrolysis curves of lead derivatives. 1) PbO from the metal. 2) PbO from the oxide PbO_2. 3) PbO from the oxide $Pb_5O_7 \cdot 3H_2O$. 4) PbO from the oxide Pb_3O_4. 5) PbO from the hydroxide. 6) Chloride. 7) Iodate. 8) Periodate. Reproduced from C. Duval, "Thermogravimetric Analysis", Elsevier Publishing Co., Amsterdam (1953), p. 463. Thanks is given to the Elsevie Publishing Co. for permission to reproduce material from this book.

4. Pyrolysis curves of lead derivatives. 9) Sulphide. 10) Sulphi 11) Hydrogen phosphate. 12) Carbonate. 13) Basic thiocyanate. 14) Oxalate. 15) Phthalate. Reproduced from C. Duval, "Thermogravimetric Analysis", Elsevier Publishing Co., Amsterdam (1953), p. 466.

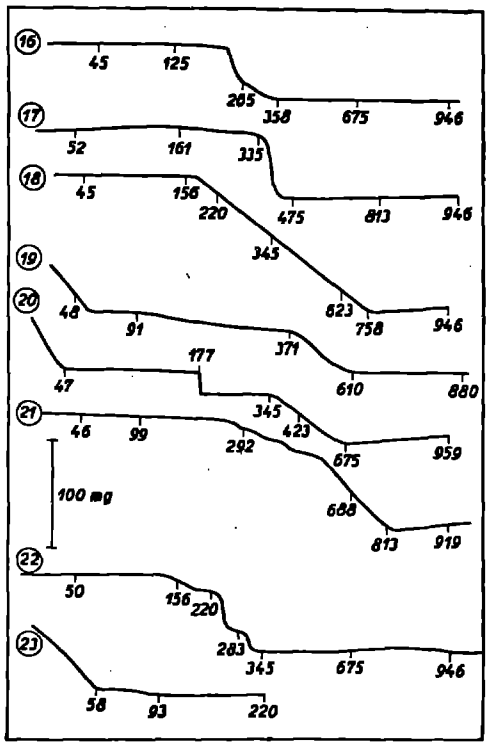


Figure 5

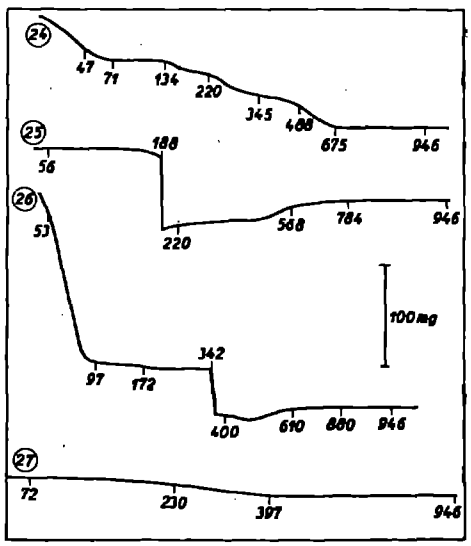


Figure 6

5. Pyrolysis curves of lead derivatives. 16) Gallic acid compound. 17) Salicylate. 18) Anthranilate. 19) Dimethylglyoxime complex 20) Salicylaldoxime complex. 21) Oxine complex. 22) 5,7-Dibrom oxine complex. 23) Picrolonic acid complex. Reproduced from C. Duval, "Thermogravimetric Analysis", Elsevier Publishing Co., Amsterdam (1953), p. 469.

6. Pyrolysis curves of lead complexes with: 24) Thionalide. 25) Mercaptobenzothazole. 26) Mercaptobenzimidazole. 27) 27-Nit 5-sulpho-oxine. Reproduced from C. Duval, "Thermogravimetric Analysis", Elsevier Publishing Co., Amsterdam (1953), p. 472.

TABLE XV

Lead Compounds Suitable for Gravimetric Determination. Preferred Compounds are Indicated by an Asterisk.

Precipitating Reagent	Form Weighed	Analytical Factor	Temperature Limits
Hydrogen	PbO	0.9283	>946°
Chlorine + Sodium Hydroxide or Electrolysis	PbO	0.9283	>650°
Hydrogen Peroxide	PbO_2	0.8662	100-120°
*Aqueous Ammonia	$Pb(OH)_2$	0.8589	155-410°
Electrolysis	PbO_x	0.8627	<340°
Hydrochloric Acid	$PbCl_2$	0.7450	In the cold
*Iodic Acid	$Pb(IO_3)_2$	0.3153	<400°
Hydrogen Sulfide	PbS	0.8659	97.5-107.2°
Sulfite, Hydrogen Sulfite or Pyrosulfite	$PbSO_3$	0.7213	<60° and >900°
*Sulfuric Acid	$PbSO_4$	0.6832	271-959°
*Potassium Sulfate	$PbSO_4 \cdot K_2SO_4$	0.4339	40-906°
Disodium Hydrogen Phosphate	$Pb_2P_2O_7$	0.7009	>355°
*Disodium Hydrogen Arsenate	$PbHAsO_4$	0.5980	81-269°
*Sodium Carbonate	$PbCO_3$	0.7754	<142°
*Sodium Chromate	$PbCrO_4$	0.6411	94-904°
Ammonium Thiocyanate	Pb(OH)CNS	0.7340	In the cold
Molybdophosphoric Acid	$Pb_{25}Mo_{25}H_{14}P_2O_{112}$	0.5480	>436°
*Oxalic Acid	PbC_2O_4	0.7018	50-300°
Sodium Phthalate	$C_2H_4(CO_2)_2Pb$	0.5580	288-320°
Gallic Acid	$C_3H_2O_3 \cdot CO_2Pb_2$	0.7138	<152°
Sodium Anthranilate	$Pb(C_7H_8O_2N)_2$	0.4322	<198°
Anthranilic Acid (Ref. F4)	$Pb(C_7H_8O_2N)_2$	0.4323	105°
Dimethylglyoxime	$Pb(OH)_2PbC_4H_6O_2N_2$	0.7598	60-88°
8-Hydroxyquinoline (Oxine)	$Pb(C_7H_6ON)_2$	0.4181	In the cold
5, 7-Dibromo-oxine	$Pb(C_7H_4ONBr_2)_2$	0.2554	In the cold
Picrolonic Acid	$Pb(C_{10}H_7O_5N_4)_2$	0.2725	58-112°
Picrolonic Acid (Ref. F4)	$Pb(C_{10}H_7O_5N_4)_2 \cdot 1.5H_2O$	0.2720	130-140°
*Salicylaldoxime	$PbC_7H_5O_2N$	0.6053	45-180°
*Thionalide	$Pb(C_{12}H_{10}NS)_2$	0.3279	71-134°
*Mercaptobenzothiazole	$Pb(C_7H_4NS_2)_2$	0.5309	<120°
*Mercaptobenzimidazole	$PbOHC_7H_7N_2S$	0.5549	97-172°
7-Nitro-5-sulfo-oxine	$Pb(C_9H_5O_5N_2S)_2$	0.2778	<48°
Diallyldithiocarbomido-hydrazine (Ref. D2)	$Pb(C_8H_{12}N_4S_2)$	0.4757	105°

Unless noted otherwise the temperature limits shown are from Reference D3.

5. Complex ions and chelate compounds.

Lead complexes play a dominant role in its separation and determination. The most important nonorganic lead complexes are those formed with halides and the hydrolyzed complexes formed in alkaline solution.

Lead is only slightly soluble in dilute acidic chloride solutions but as the chloride ion concentration increases the solubility becomes greater. The solubility of lead chloride

reaches a minimum at about 1 M hydrochloric acid in sodium or lithium chloride (D4). Ion exchange absorption measurements (N2) also show that lead ions become predominantly negative in about 2 N hydrochloric acid. The complexes formed are probably either $PbCl_3^-$ or $PbCl_4^=$ or both. There is considerable other evidence for the existence of these complex ions but their stability constants have not been determined. Nelson and Kraus (N2) postulate the existence of a $PbCl_5^{-3}$ complex at high hydrochloric acid concentration in spite of the usual assignment of a coordination number of four for lead.

The existence of a mononitrate complex of lead, $PbNO_3^+$, has been established (H8). That formation of negatively charged nitrate complexes does not take place to any considerable extent is indicated by the failure of lead nitrate to increase in solubility with increasing nitrate concentration (S4). The absence of such complexes is also shown by the failure of lead nitrate to absorb appreciably on anion exchange resins from nitric acid or ammonium nitrate solutions (N2) and by the non-extractability of lead into diethylether from nitrate solutions (B1).

The formation of plumbite ions $HPbO_2^-$ in strongly alkaline solutions has already been noted in section IV-4. This complex plays an important role in some separation processes. A few other inorganic complexes such as the selenocyanates, $Pb(CNSe)_3^-$ and $Pb(CNSe)_6^{4-}$ are known (G1)(G2) but have not been important for lead analysis.

Lead forms complex ions or chelate compounds with many organic reagents. Some of the complexes which are insoluble in aqueous solution have been used in separation processes and have been discussed in section IV-4. Others produce quantitative and selective extraction into organic solvents, and selective adsorption on ion exchange resin, inorganic exchangers or on filter paper. Some act as masking agents in extraction,

electrochemical, or precipitation separations. These effects are discussed in other parts of this review. The formation constants (or stability constants) for a number of organic complexes are summarized in Table XVI. The formation constant is taken as the equilibrium constant for the reaction in which the metal chelate is formed from the hydrated metal ion and the

Table XVI

Formation Constants of Lead Chelate Complexes.

Ligend	Abbreviated Formula	Metal Chelate	$\log_{10}K$	Temp °C	Ionic Strength
Tartaric Acid	H_2A	MA	-2.91	25	0.1
	$H_2A(OH)_2$	$M(HAO)(OH)_2$	14.5	25	0.1
Acetic Acid (Ref. 87)	HA	MA	3.87	25	
Citric Acid	H_3A	MHA	-2.11	25	0.05
		MA	5.74	25	0.16
Malonic Acid (Ref. 88)	H_2A	MA	4.35	25	
Phthalic Acid (Ref. K6)	H_2A	MA	2.19	25	1.0
		MA_2	3.41	25	1.0
8-Hydroxyquinoline-5-sulfonic acid	H_3A	MA	8.53	25	0
Mercaptoacetic acid	H_2A	MA	8.50	25	0.15
		MA_2	7.6	25	0
Nitroacetic acid	HA	MA	0.14	18	0.6
2-Mercaptoethylamine	H_2A	MA	11.10	25	0.15
Glycine	HA	MA	5.47	25	0
		MA_2	3.39	25	0
α-alanine	HA	MA	5.00	25	0
		MA_2	3.24	25	0
Cysteine	H_2A	MA	12.20	25	0.15
Methionine	H_2A	MA	4.40	25	0.15
Histidine	H_2A	MA	6.84	25	0.15
Glutathione	H_2A	MA	10.6	25	0.15

Table XVI (con't)

Ligend	Abbreviated Formula	Metal Chelate	$\log_{10}K$	Temp °C	Ionic Strength
Glycylglycine	H_2A	MA	3.23	25	0
		MA_2	2.70	25	0
Anilinediacetic acid	H_2A	MA	3.49	20	0
N-Acetamidoiminodiacetic acid	H_2A	MA	8.40	20	0.1
		MA_2	2.24	20	0.1
β-(N-Trimethylammonium) ethyliminodiacetic acid	H_2A	MA	5.40	20	0.1
N-Methoxyethyliminodiacetic acid	H_2A	MA	9.49	20	0.1
		MA_2	3.75	20	0.1
		MAOH	-10.11	20	0.1
		MA_2OH	-10.72	20	0.1
N-Hydroxyethyliminodiacetic acid	H_2A	MA	9.41	20	0.1
		MA_2	4.17	30	0.1
		MAOH	-8.25	20	9.1
β-Mercaptoethyliminodiacetic acid	H_3A	MA	17.03	20	0.1
N-Methylthioethyliminodiacetic acid	H_2A	MA	9.12	20	0.1
		MA_2	3.36	20	0.1
		MAOH	-10.44	20	0.1
Nitrilotriacetic acid	H_2A	MA	0.54	20	0.1
Ethylenediamine-N, N-diacetic acid	H_2A	MA	12.22	20	0.1
		MA_2	2.90	20	0.1
Ethylenediaminetetraacetic acid (EDTA)	H_4A	MA	18.04	20	0.1
		MHA	5.02	20	0.1
1,2-Diaminocyclohexane-N, N'-tetraacetic acid	H_4A	MA	19.68	20	0.1
		MHA	5.18	20	0.1
Ethylenediamine-N, N'-Dipropionic-N, N'-diacetic acid	H_4A	MA	13.2	30	0.1

Unless noted otherwise these values are taken from reference C1.

most highly dissociated form of the chelating agent.

$$M^{+n} + A^{-m} \quad MA^{n-m} \quad K_{MA} = \frac{[MA^{n-m}]}{[M^{+n}][A^{-m}]}$$

An extremely important lead complex is that formed with diphenylcarbazone (dithizone). This complex is used in lead separations and is the basis for the most important colorimetric method for lead (see section IV-6).

6. Analytical determinations other than gravimetric.

The interest of radiochemists in other than gravimetric methods for determining chemical yields has been increasing over the past few years. The impetus for this interest arises largely from (1) a desire for increased speed, convenience and precision or (2) the desire to work with very small amounts of material, (micrograms instead of the 5-50 milligrams usually required by the gravimetric methods). The determination of the yields of constituents of a mixture can also be useful, allowing simple and fast group separations to be performed from complex mistrues of radioelements followed by measurement of the groups without further separation by gamma ray spectral analysis or gamma ray and beta particle decay analysis.

A. Volumetric methods.

According to Hillibrand and Lundell (H3) the best of the volumetric methods for lead is precipitation of lead chromate from acetic acid solution, dissolution of the washed precipitate in hydrochloric acid, addition of excess potassium iodide and titration of the liberated iodine with a standard sodium thiosulfate solution. This procedure has recently been reviewed by Ryazanov (R2).

Due to the tendency of lead to form stable complexes with many organic molecules a number of volumetric procedures

involving compleximetric titrations have been developed. The indirect method of Vancea and Volusniuc (V2) utilizes the precipitation of the phosphate from a lead acetate solution in the presence of a chloroform solution of dithizone. The titrant is a standard solution of potassium phosphate. At the equivalence point (when an excess of phosphate ion is introduced) the color of the chloroform fraction changes from red to green. The authors indicate that the method is as accurate and reproducible as gravimetric methods. It has little to offer to the radiochemist, however, in terms of sensitivity or convenience.

Direct compleximetric titratron of lead with 0.07 N complexon III in the presence of Erichrome Black T as an indicator has been proposed (Z1). The equivalence point is reached when the color changes from violet to bluegreen. X-ylenol orange and methyl thymol blue have been used as indicators with Trilon as titrant (K4). After precipitation of lead sulfate and dissolution in ammonium acetate the indicator was added and the solution titrated. With X-ylenol orange the pH should be 5.4-5.9 and the color change is from violet-red through pink, pinkish orange and orange to yellow at the end point. With methyl thymol blue the pH should be 5.7-6.5 and the color change is from blue through violet, pink to yellow. Elements coprecipitated with lead sulfate are said not to interfere (K4).

The most sensitive and perhaps for the radiochemist, the most useful volumetric procedure is complexiметric titration utilizing the lead EDTA complex. A number of indicators have been used for the direct EDTA titration (W5). The most popular of these are Eriochrome Black T (C1)(W5), Eriochrome Red B and X-ylenol orange (W5). The direct titration with the sodium salt of EDTA is carried out in a pH 10 buffer solution (F5)(F6). Iron, the alkaline earths and the earths interfere but bismuth, aluminum and antimony do not. Cyanide can be used to mask cobalt, nickel, copper, zinc, cadmium, mercury and platinum (C1).

The use of X-ylenol orange as an indicator in acid solution is one of the most sensitive of the volumetric methods, allowing microgram quantities to be determined (W5). Care must be taken, however, due to avoid the presence of other heavy metals which may intefere. Indirect methods of titration using EDTA have been proposed (C1) but these normally lack the sensitivity of the direct method.

Potentiometric or amperometric titrations of lead using EDTA titrant have been used (W5)(C1). These can be quite sensitive but are not as convenient as other methods and leave the lead in a poor state for measurement of its radioactivity since a mercury electrode is usually used (C1). Milligram quantities of lead have been determined by high frequency titration using standard solutions of potassium dichromate, and ammonium chromate as titrants (M22). This method suffers from inconvenience for occasional use and leaves the lead in the form of a precipitate. For routine use such a procedure followed by quantitative transfer of the precipitate to a filter paper might be used to avoid weighing errors or to check weights.

The volumetric methods of determination have been little used by the radiochemist and will probably remain so. Certain special conditions may warrant their use so they have been reviewed briefly.

B. Colorimetric methods.

Colorimetric determinations have been used occasionally in the past by radiochemists (Cf. ref. M6, H16). It is expected that as the techniques requiring the use of very small amounts of carrier material, such as four pi beta particle, or gamma ray counting, become more widely used, the high sensitivity and precision of colorimetric methods will become more attractive to radiochemists. The normal limits of sensitivity for colorimetric methods are in the range of 10^{-7} grams although some methods for

lead are very sensitive and allow measurements in the range 10^{-8}-10^{-9} grams to be made (S5). In terms of sensitivity, convenience, selectivity, and precision, spectrophotometric methods are generally superior to comparative colorimetry. Also, the subjectiveness of the spectrophotometric determination adapts it well to both routine and occasional analysis. Therefore, in spite of the higher cost of spectrophotometric equipment, this method is recommended and is the one primarily considered in this review.

1. Dithizone.

Dithizone is the outstanding reagent for colorimetric determination of traces of lead. This reagent has attained prominence in lead chemistry due not only to the sensitivity of the determination but also to the selectivity with which the lead dithizone complex can be extracted into organic solvents. The solvents usually employed for the extraction as well as the determination are carbon tetrachloride or chloroform (S5) although toluene has also been used (S6). Carbon tetrachloride is probably to be preferred for this application. An objection in some cases to the use of carbon tetrachloride instead of chloroform is the limited solubility of dithizone in carbon tetrachloride. In some cases, however, the absence of a large excess of dithizone in the organic phase is an advantage. The use of dithizone for separations is discussed in detail in section IV-7.

Lead dithizonate in carbon tetrachloride gives a distinctive red color. The wavelength used for the determination is 520 mm with an extinction coefficient ε = 66,500. The absorption curve for lead in carbon tetrachloride is shown in Figure 7. The absorption curves of dithizone and its oxidation product are shown in Figure 8. It will be seen from Figure 8 that there is a minimum in the dithizone absorption curve at about 510 mμ which is close to the

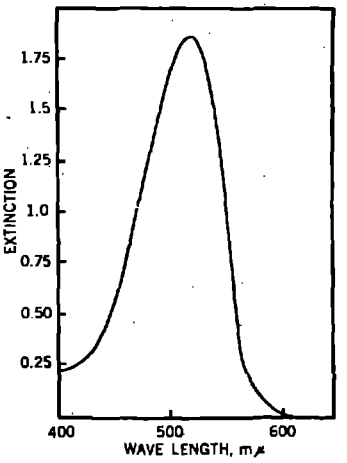


Figure 7

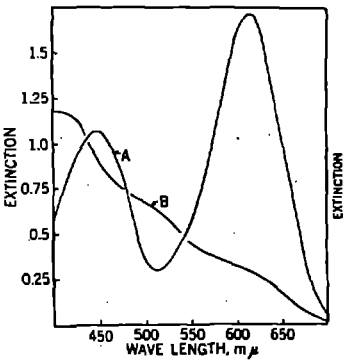


Figure 8

7. Absorption curve for lead dithizonate in carbon tetrachloride. From E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience Publishers Inc., New York (1959), p. 166. Thanks is given to the copyright holders, Interscience Publishers and to Professor Sandell for permission to reproduce material from this book.

8. Absorption curves for: A. dithizone, and B. its oxidation product, both in carbon tetrachloride solution. From E. B. Sandell, "Colorimetric Determination of Traces of Metals, 3rd Ed., Interscience Publishers Inc. (1959), p. 165.

wavelength of maximum absorption of lead (Figure 7). On the other hand, lead dithizonate absorbs very little light above 600 mu whereas the strongest absorption is shown by dithizone at approximately 620 mu. The amount of lead may therefore be measured by the absorption of light by the lead dithizonate complex at 520 mu (usually preferred) or by the absorption of light by the excess of dithizone remaining after the reaction is completed.

The solubility of dithizone in aqueous solution increases with the pH of the solution. When one works in alkaline medium it is possible to transfer virtually all the excess dithizone to the aqueous phase. Therefore one can extract lead practically completely from an aqueous medium of pH 11 without extracting an

appreciable amount of dithizone when carbon tetrachloride is used as solvent (S5). Another frequently used procedure is to measure the intensity of the excess dithizone absorption at 620 mu and correct the measurements of the lead complex at 520 mu for contributions due to excess dithizone.

The presence of the oxidation product of dithizone can lead to errors in the determination since it adsorbs in part at the wave length of interest. Dithizone is oxidized by ferric iron, especially in basic solution. Free halogens, nitrous acid or permarganate ion also cause some oxidation. The oxidation can be prevented in large measure by adding hydroxylamine hydrochloride to the aqueous solution to be extracted.

It is frequently necessary to purify commerical dithizone before using it for colorimetric determination. This can be easily done by crystallization from chloroform. The chloroform-dithizone solution is heated to 40° in a steam of filtered air (or nitrogen) until about half of the dithizone has precipitated (ref. S5, p. 171). Dithizone solutions prepared from purified chloroform or carbon tetrachloride can be kept for several months when stored at 40°F in the dark (S5). Carbon tetrachloride solutions are stabilized by covering with a 0.1 M solution of sulfur dioxide in water.

The final colorimetric determination of lead is usually done by extracting the lead from an ammonia-cyanide-sulfite solution into 0.001% w/v dithizone solution in carbon tetrachloride.

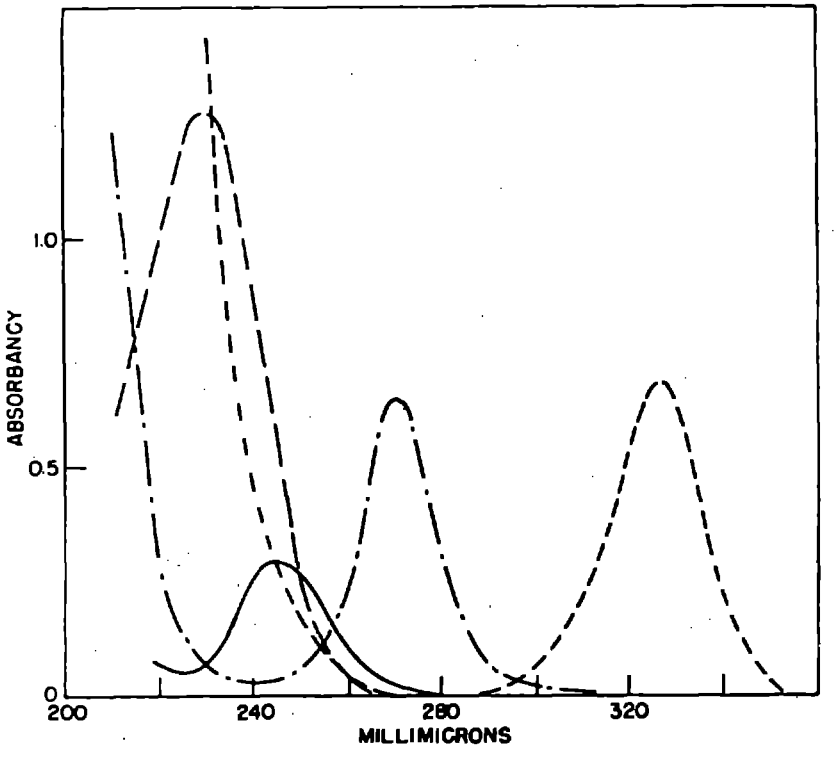
2. Other colorimetric reagents.

Di-β-naphthylthiocarbazone which forms a distinct purple complex with lead has been used for its colorimetric determination (H7). This reagent appears to be similar to dithizone in its sensitivity. It has no apparent advantages over dithizone for lead determinations and is somewhat harder to obtain in pure form.

Lead can be determined colorimetrically by electrolytic deposition as dioxide followed by oxidation of tetramethyldiaminodiphenylmethane by the dioxide to an intensely colored blue diphenylmethane dye (S5). It may be used for amounts of lead above 5γ. This method would appear to have limited application. However if an electrodeposited lead dioxide deposit is used as a method of mounting a lead sample for measurement of its radioactivity this may be a useful method of subsequently determining its lead content.

The absorption spectra of the halide complexes of thallium, lead and bismuth have been investigated by Merritt, Hershenson and Rogers (M7). The chief advantage of this method as far as the radiochemist is concerned would probably be the possibility of determining these three elements together. In some cases further separation is not necessary since gamma ray energy spectra or decay analysis will allow adequate measurement of the isotopes of interest. Of the halide complexes, the chloride showed the largest separation of the absorption peaks. The absorption curves for thallium, lead and bismuth from reference (M7) are shown in Figure 9. A simple group separation of these three elements from complex mixtures can be made by extraction into dithizone from cyanide medium (see section IV-7). Only tin (II) co-extracts. The ions can then be re-extracted into 1:1 hydrochloric acid solution and their concentrations determined by measuring the absorbancy at 245 mu for thallium, 271 mu for lead and 327 mu for bismuth. Interference from tin can be minimized by oxidation to tin (IV).

A water soluble chelate complex between lead and 4-(2-pyridylazo)-resorcinol which is useful for the spectrophotometric determination of lead has been described by Pollard, McOmie and Nickless (P1). Their procedure is to add 2 ml of a 0.05% w/v aqueous solution of the reagent plus 10 ml of a pH 10 buffer solution (ammonium chloride-ammonium hydroxide) to the



9. Absorption spectra of 10 p.p.m. bismuth (III), mercury (II), lead (II) and thallium (I) in 6 M hydrochloric acid.

———— Thallium

— — — — Mercury

— - — Lead

- - - - - Bismuth

From C. J. Merritt, H. M. Hershenson and L. B. Rogers, Anal. Chem. 25, 572 (1953).

neutral solution of the lead in a 25 ml volumetric flask. After dilution to 25 ml the optical density of the solution is measured at 530 mu against a blank solution containing no lead. They report that Beer's law is obeyed up to five micrograms of lead per ml.

Ultraviolet spectrophotometric determination of lead has carried out in perchlorate solutions (I3). Lead shows maximum absorption at 208 mu in acid solution and at 240 mu in alkaline solution. Iron (III), bismuth, antimony and tin and

various anions interfere. Compared to the dithizone system this system holds little promise analytically.

The absorption spectra of lead and bismuth EDTA complexes in 0.01 M perchloric acid are described by Welcher (W5). Both the lead ion and its EDTA complex are colorless but they show strong absorption bands in the ultraviolet. Unlike the strong shift in the absorption peak of lead ions in perchloric acid produced by the presence of various anions (I3) the EDTA complex shows no such dependence. Maximum absorption for the lead-EDTA complex occurs at 240 mu. Lead concentrations down to 10^{-6} M can be determined. The absorption curves for the EDTA complexes of lead and bismuth and of the uncomplexed ions in 0.01 M perchloric acid are shown in Figure 10. Lead and bismuth can be determined simultaneously by titrating a mixture of the ions in perchloric acid with dilute EDTA solution and measuring the absorbancy change of 240 mu ultraviolet light on a spectrophotometer (W5). The more stable bismuth-EDTA complex forms first followed by the lead complex. A titration curve showing the sharp end points obtained is shown in Figure 11.

C. Polarography.

Of the various methods of determination of trace amounts of material, pology has perhaps been most neglected by the radiochemist. This method is one of the best for determination of the concentration of the constituents of mixtures combining high sensitivity with speed and precision. Polarography is also easily adapted to automatic operation and to remote handling of radioactive solutions. The determination is probably best carried out on an aliquot of the sample with radiation measurement on a separate aliquot. A comprehensive review of the principles and applications of polarography is available (K5).

The chemical and electrochemical characteristics of lead are very favorable for its polarographic determination.

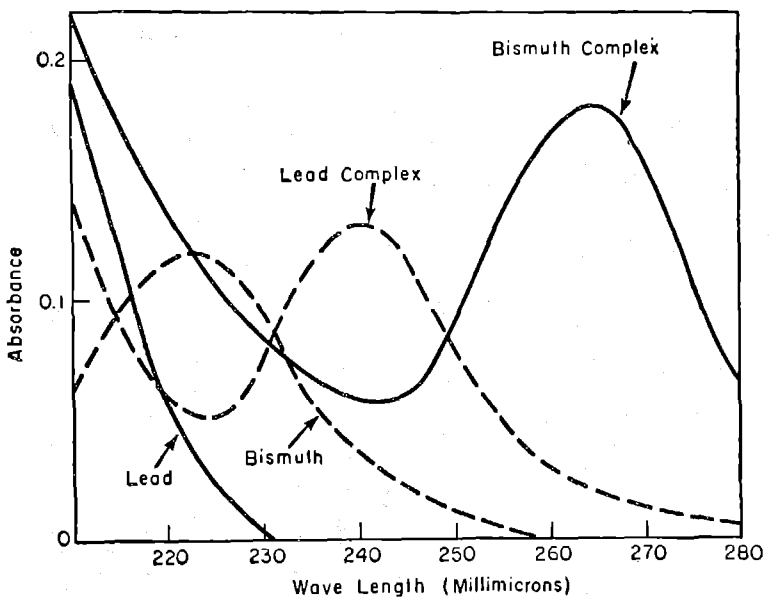


Figure 10

Absorption spectra of bismuth and lead perchlorates and their EDTA complexes. Concentration of bismuth and lead and their complexes is 2 x 10^{-5} M in 0.01 M perchloric acid. From F.J. Welcher, "The Analytical Uses of Ethylenediaminetetra-acetic Acid", D. Van Nostrand Co., Inc., Princeton, N. J. (1958), p. 83. Thanks is given to the publishers for permission to reproduce material from this book.

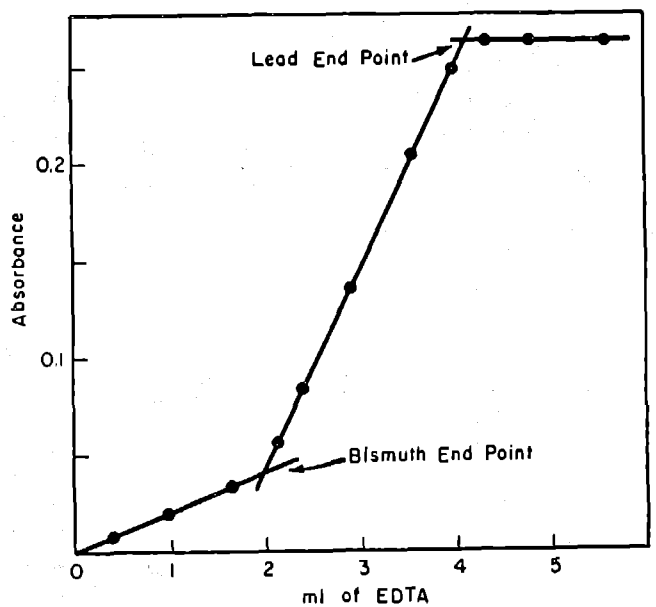


Figure 11

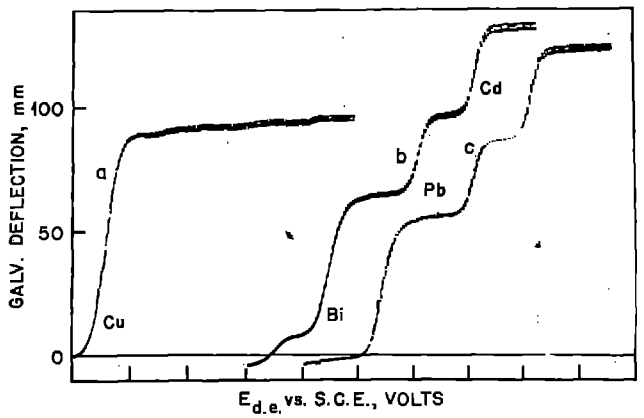
Titration curve for simultaneous titration of lead and bismuth with EDTA (0.5 mg of Bi and 0.5 mg of Pb titrated at 240 mμ). From F. J. Welcher, "The Analytical Uses of Ethylenediaminetetra-acetic Acid", D. Van Nostrand Co., Inc. Princeton, N. J. (1958), p. 83.

The polarographic characteristics of lead in various supporting electrolytes at 25° are shown in Table XVII.

Table XVII
Polarographic characteristics of lead in various supporting electrolytes at 25°C.

Supporting Electrolyte	$E_{1/2}$ vs. S.C.E., V.	Diffusion Current Constant I
0.1 M KCl (or HCl)	-0.396	3.80
1 M HCl (or KCl)	.435	3.86
1 M HNO_3	.405	3.67
1 M NaOH	.755	3.39
0.5 M tartarate, pH = 4.5	.48	2.37
0.5 M tartarate, pH = 9	.50	2.30
0.5 M tartarate + 0.1 M NaOH	.75	2.39

Sodium hydroxide supporting electrolyte is especially useful for the determination of lead in the presence of tin, antimony and arsenic. Stannite ion and arsenite ion do not show reduction waves in this medium and the half-wave of antimonite is 0.5 V more negative than that of plumbite (K5). Tartarate is recommended as a supporting electrolyte for the simultaneous determination of copper, bismuth, lead and cadmium (K5). The waves are in the order listed and are best separated at a pH between 4 and 5 (L4). The polarograms of a copper, bismuth lead, and cadmium mixture taken from reference (L4) is shown in Figure 12. This is representative of the separations observed in lead mixtures. Curve A of this figure indicates the situation in the presence of a large excess of copper. As noted in the caption, most of the copper was removed by electrolysis and the polarogram of the mixture is shown on curve D. That the copper electrolysis did not remove significant amounts of the other constituents is shown by comparing curve B with curve C which is a polarogram of an identical mixture except copper was absent in this case.



12. Polarogram of copper, bismuth, lead and cadmium mixture in a tartarate supporting electrolyte at pH 4.5. (a) with large excess of copper. (b) polarogram of solution from a at higher sensitivity after electrolysis of copper at -0.13 to -0.16 v vs. S.C.E. (c) solution containing same concentrations of bismuth, lead and cadmium as in solution a. From J. J. Lingane, "Electroanalytical Chemistry", Interscience Publishers Inc., New York (1953), p. 327. Thanks is given the publishers and Professor Lingane for permission to reproduce material from this book.

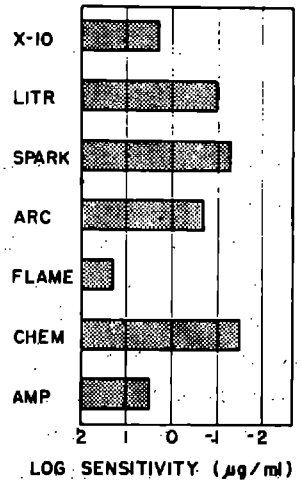
A cyanide supporting electrolyte is useful for determining lead in the presence of large amounts of cadmium because the wave of the lead-cyanide complex precedes that of the cadmium complex by about 0.4 V (K5). Bismuth, antimony, lead and tin mixtures have been determined using a hydrochloric acid-sodium fluoride supporting electrolyte (L6). The use of an ammoniacal tartarate soln has been found to be beneficial for the simultaneous determination of thallium and lead (B2).

The sensitivity of polarographic determinations can be extended into the 10^{-8} M range by application of the recently developed square-wave polarographic techniques. Milner and Slee have used this method with an orthophosphoric acid base to determine trace quantities of lead in monzanite and in various copper, tin, zinc and aluminum base alloys (M8).

Using a mercury plated platinum electrode, Marple and Rogers have devised a fast coulometric method for determination of trace concentrations of lead down to 10^{-8} M (M9).

D. Comparison of the sensitivity of various determination methods.

It is of interest to compare the sensitivity of the various methods for determination of lead. Figure 13 shows



13. Graph comparing sensitivity of determination methods for lead. Various methods are discussed in text. From W. W. Meinke, Science 121, 177 (1955).

the results of such a comparison by Meinke (M10). The first two bar graphs indicate the sensitivity by neutron activation using a 5 x 10^{11} neutrons/cm^{-2} sec^{-1} flux (X10) and a 1 x 10^{13} neutrons/cm^{-2} sec^{-1} flux (LITR). The other determination methods indicated are: spark, copper spark method of spectrographic analysis; arc, graphite D-C arc method of spectrographic analysis; flame, flame spectrometer analysis with an oxyhydrogen flame; chem, sensitive color reaction using a one centimeter cell; and amp, amperometric titration. The high sensitivity of the colorimetric method for lead is apparent from this graph.

7. Solvent Extraction

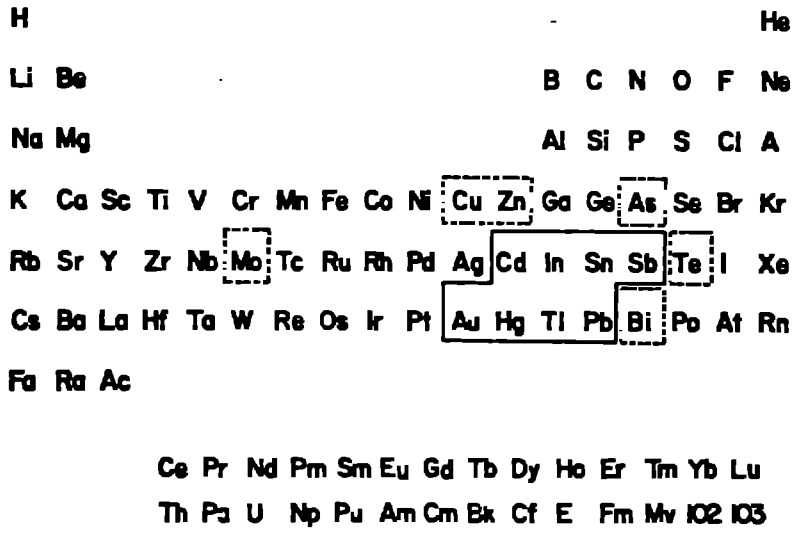
Solvent extraction has proved to be a valuable tool in radiochemical and analytical studies of lead. The most widely used extraction system uses the extraction of the dithizone

complex into carbon tetrachloride or into chloroform. The popularity of this method is due in part to the utility of dithizone as a colorimetric indicator for lead. Extraction of many other complexes have been studied, some of which show considerable promise for radiochemical application. Two reviews of solvent extraction by Morrison and Freiser (M1, F1) have recently appeared.

A. Ion association systems.*

Iodide

Of the simple ionic systems, solvent extraction of the iodide is the most useful for lead. Lead is extracted from acidic iodide solutions into methyl isopropyl ketone (W1)(W2). The elements extracted from acidic iodide solutions with various solvents are shown in Figure 14. Elements partially or com-



14. Elements extracted into iodide system. Solid blocks - appreciably extracted, broken blocks - partially extracted. From H. Freiser and G. H. Morrison, "Solvent Extraction in Radiochemical Separations", Ann. Rev. of Nuc. Science 9, 221 (1959). Thanks is given the publishers and Professor Freiser for permission to reproduce material from this article.

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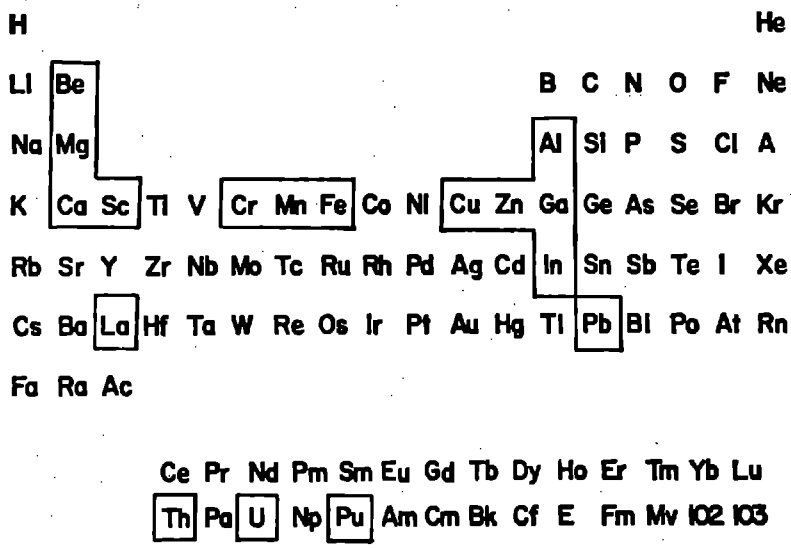
* This classification follows Freiser and Morrison (F1).

pletely extracted by methyl isopropyl ketone are tin (IV), mercury (II), iron (III), antimony, copper, palladium, cadmium, rhodium, gold and ruthenium (W1)(W2). Most of these elements can be removed by a preliminary extraction with the solvent from thiocyanate or hydrochloric acid media. Iron, copper, zinc, mercury, gold and palladium are completely extracted as their thiocyanates while tin and antimony are extracted as chlorides. The preliminary extraction can be carried out from a saturated ammonium thiocyanate - 5% hydrochloric acid solution. By adding saturated potassium iodide solution to the aqueous phase lead can then be extracted. Copper and ruthenium extract with the lead. There is some question about the behavior of bismuth through this procedure. West (W1) reports that bismuth is separated from lead. However, Morrison and Freiser (M1) indicate that bismuth is extracted into methyl isopropyl ketone. The extraction of bismuth from iodide solutions into methyl isobutyl ketone has also been observed (W3). If a bismuth separation is desired, this point would seem to require further investigation.

Carboxylic Acids

Figure 15 shows the elements extracted from alkaline aqueous solutions by carboxylic acids dissolved in organic solvents. The solvent preferred is methyl isobutyl ketone. This figure is from the review of Freiser and Morrison (F1). The details of the extraction are not clear from this review nor do the references given give details for extraction of any elements except chromium. From the figure this appears to be an attractive system for lead separations.

Using perfluorooctanoic acid in nitrate and perchlorate solutions, divalent cations (CaII, MgII, FeII, PbII and ZnII) have been separated from monovalent cations by Mills and Whetsel (M2). The extraction proceeds best at a pH just below that which



15. Elements extracted in carboxylic acid systems. From H. Freiser and G. H. Morrison, "Solvent Extraction in Radiochemical Separations", Ann. Rev. of Nuc. Science 9, 221 (1959).

would cause formation of the insoluble hydroxide of the metal of interest.

Extraction of Contaminants from Lead

Due to the failure of lead to extract into organic solvents from hydrochloric or nitric acid solutions (W2)(B1)(F1), such systems are useful for removal of large amounts of target material prior to lead separation or to remove major active species to permit easier and safer handling. Although less satisfactory than a selective separation of lead these systems can also be used for final purification of lead samples from certain contaminants. P. W. West and coworkers (W1)(W3) and T. S. West (W2) have found that copper, iron, zinc, antimony, tin (IV), mercury (II), platinum, gold, palladium and rhodium can be removed from dilute hydrochloric acid solutions containing an excess of ammonium thiocyanate by extraction with methyl isopropyl ketone leaving lead in the aqueous phase. Thallium can also be removed by adding bromine water to the

solution prior to the extraction. Two passes with the ketone not only removes the metal chlorides and thiocyanates but also removes excess bromine.

According to figure 10 of reference F1, bismuth can be separated from lead in acid media by extraction with a 0.1 M solution of either tri-n-octylphosphine oxide or 2-ethyl-n-hexyl phosphine oxide in cyclohexane.

A convenient method for removing polonium from bismuth or lead has been patented by Karraker (K1). The polonium is removed from dilute hydrochloric acid solution by extraction with tributyl phosphate ether or by a 20% solution of tributyl phosphate in dibutyl ether (H9).

Thorium, bismuth and polonium can be quantitatively separated from lead (and radium) by extraction from a saturated aluminum nitrate solution with mesityl oxide (M3). Thallium can be separated by extraction of thallium III into a solution of 5% n-octanol in hexone from 0.15 M hydrochloric acid (L2). It may be necessary in some cases to add an excess of bromine water to oxidize the thallium prior to the extraction. This is a convenient method for separating lead from thallium target material.

B. Chelate systems.

Dithizone

Diphenylthiocarbazone, or dithizone,

$$S = C\begin{matrix}\diagup NH\text{-}NH\text{-}C_6H_5 \\ \diagdown N{=}N\text{-}C_6H_5\end{matrix}$$

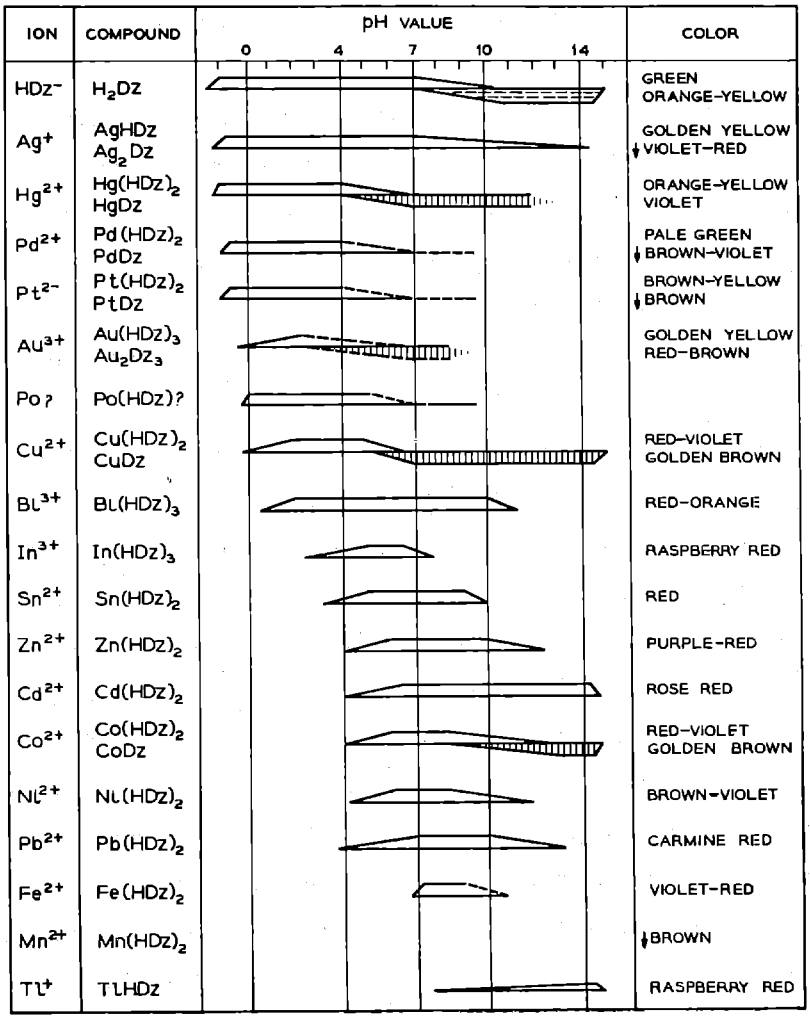
has played a prominent role in lead chemistry for twenty years and it is not expected that its use will diminish. As noted in section IV-B the sensitivity of the dithizone colorimetric method for lead equals and even exceeds that of spectrographic methods. Dithizone is valuable for isolation of lead from a large variety of mixtures because of the selectivity of extraction

of lead dithizonate into organic solvents. The literature on the application of dithizone to lead separation and determination is extensive. Only representative cases will be considered in this review.

Dithizone is a velvet-black solid which dissolves in most organic solvents to greater or lesser extent. Carbon tetrachloride or chloroform are the solvents used almost exclusively in analytical applications. The room temperature solubility of dithizone in chloroform is about 2 grams per 100 ml and in carbon tetrachloride about 0.05 grams per 100 ml. Dilute solutions of dithizone in both these solvents are green in color.

It is usually necessary to purify commercial dithizone before use (due to oxidation). If a 0.01% solution in carbon tetrachloride is shaken with dilute (1:100) ammonium hydroxide and only a faint yellow color remains in the organic layer, it may be used without further purification. Dithizone purification can be accomplished by the following simple procedure (M1): dissolve about 1 g. dithizone per 100 ml chloroform and filter off residue. Extract dithizone into several 100 ml portions of redistilled 0.2 M ammonium hydroxide. Acidify the ammonia solution with dilute hydrochloric acid, precipitating the dithizone. Extract the precipitate into a minimum amount of chloroform and evaporate chloroform in a stream of filtered air (or preferably nitrogen gas). Store reagent in a dark bottle.

Figure 16 adapted from the recent review of Iwantscheff (I4) shows the pH dependence of the extraction of eighteen metal dithizonates into carbon tetrachloride. A number of the metal dithizonates change from the primary $Me(HDz)_n$ to the secondary $Me\ Dz_{0.5n}$ form in basic solution. The utility of dithizone extractions for selective separations is not apparent from this figure except for the possibility of separating elements numbered one through eight from the remainder by extraction from acid solutions. The use of masking agents to prevent extraction of



16. Schematic representation of the pH dependence of the extraction of dithizonates in carbon tetrachloride.

↕ 100 per cent extraction of the primary dithizonates

↕ 100 per cent extraction of the secondary dithizonates

↕ 100 per cent extraction of dithizone from aqueous solution

↓ The secondary dithizonate is insoluble in CCl_4. The color given is for the aqueous suspension.

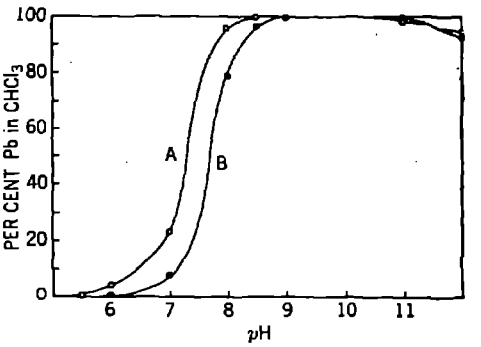
Adapted from G. Iwantscheff, Angew, Chem. 69, 472 (1957).

certain species, however, increases the selectivity to the point that complete separation of lead from almost all other elements can be achieved.

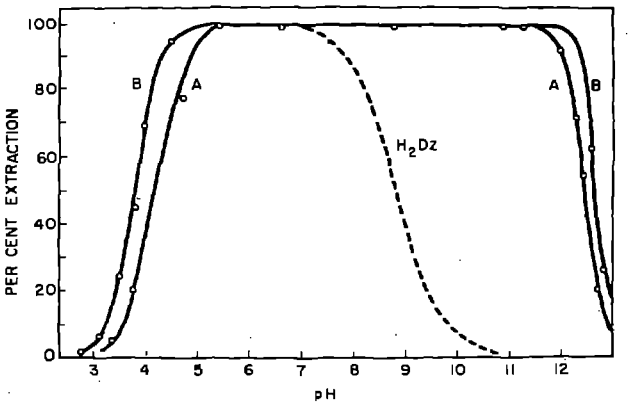
Detailed extraction curves of lead dithizonate into chloroform and carbon tetrachloride are shown in Figure 17 and Figure 18. The decision between the use of chloroform or of carbon tetrachloride as solvent in lead separations is influenced mainly by the amount of lead carrier added or the amount of lead expected. The use of carbon tetrachloride gives better separations in some cases and is preferred for the colorimetric determination because of the smaller amount of excess dithizone present (see section IV-6). The solubilities of metal dithizonates are less in carbon tetrachloride, however, than in chloroform. The solubility of lead dithizonate in carbon tetrachloride at 25° is 5.7×10^{-6} M or 1.2 p.p.m. (w/v) lead (ref. S5, p. 567). It is possible to work with carbon tetrachloride solutions which are moderately supersaturated. Thus, solutions containing up to 3.5 p.p.m. lead behave normally. If too large a sample is taken precipitation of lead dithizonate may result and is often characterized by a scum at the carbon tetrachloride aqueous solution interface. If present, this should be brought into solution, after drawing off most of the carbon tetrachloride, with fresh solvent.

Cadmium can be separated from lead by extraction from a strongly basic (1 N sodium hydroxide) solution after addition of citrate or tartarate to prevent precipitation of the metal hydroxides (V1). Cadmium is extracted, lead remains in the aqueous phase.

A powerful method of differentiating against the elements co-extracted with lead is through the use of complexing agents. For example, the only metals extracted from weakly basic (pH 8-10) medium containing cyanide are lead, thallium (I), tin (II), indium and bismuth (M1). The presence of tartarate



17. Extraction of lead dithizonate in chloroform. A. with 50% excess dithizone; B. with 25% excess dithizone. From E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience Publishers Inc., New York (1959).



18. Extraction of lead dithizonate and dithizone in carbon tetrachloride. The solid curves are for extraction of .062 mg Pb in 25 ml of aqueous solution with A. 0.001 per cent w/v dithizone in CCl_4 and B. 0.01 per cent w/v dithizone in CCl_4. From E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience Publishers Inc., New York (1959), p. 566.

or citrate, which is always added in lead separations to discourage separation of metal hydroxides, hinders indium extraction (S5). In the presence of large amounts of indium or appreciable levels of indium radioactivity it may still interfere. Since stannic tin does not extract and bismuth can be separated by extraction from slightly acidic medium the only other metal

that will interfere is thallium. EDTA prevents extraction of lead at all pH's (M1).

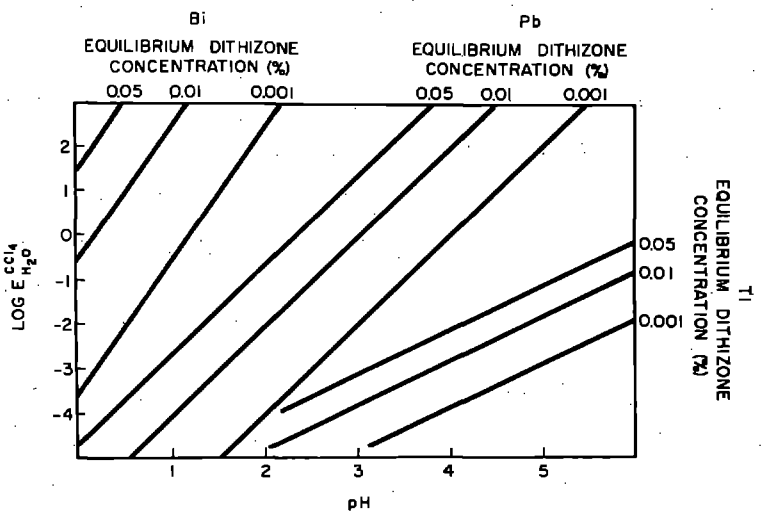
Dithizone extraction from cyanide solution has been used to advantage in a wide variety of analytical applications including separation of lead from uranium metal (C2), from antimony sulfide (N3) and from stone meteorites (R3).

A number of substances can cause interference with the basic cyanide extraction of lead. Iron (III) in alkaline cyanide medium gives ferricyanide which oxidizes dithizone (S5). If iron is present or suspected, hydroxylamine hydrochloride should be added. Copper also tends to oxidize dithizone in basic medium. In the presence of much calcium or magnesium and phosphorus, the insoluble ammonium phosphates of these salts may precipitate and carry lead strongly. For moderate amounts of these metals sodium hexametaphosphate can be added to prevent phosphate precipitation (A1). If calcium or magnesium phosphate concentrations are too high, a preliminary lead extraction with a carbamate reagent may be required (see below). Stannic acid also carries down lead and when much tin is present it must be removed, as by volatilization of the bromide (ref. S5, p. 583).

The equilibration rate for some metals (notably copper) is quite slow in acidic solutions (slower in chloroform than carbon tetrachloride) (S5). Vouk and Weber have found the equilibration of lead between carbon tetrachloride and aqueous solutions to be very rapid at all pH's (V3). Instead of extracting interfering elements from weakly acid solutions to separate from lead it is often preferable to extract from an alkaline citrate solution in which the interfering metals are co-extracted with lead. The lead is then removed from the organic phase into dilute (0.02 N) nitric acid. This is followed by addition of citrate (or tartarate) and cyanide, adjusting the pH to ~8.5 and re-extracting the lead into dithizone. This can be done only when the total amount of reacting metal is small

because of the limited dithizonate solubility in the organic phase. This method has been used to separate lead from biological samples (A1), rocks and stone meteorites (M11) and from zirconium metal and zirconium alloys (G3).

Separations from bismuth are important for many radiochemical applications. If macro amounts of either constituent is present as in the use of a lead or bismuth cyclotron target, a preliminary separation as by precipitation of lead sulfate or bismuth oxychloride may be necessary. The extraction coefficients for lead, bismuth and thallium over the pH range of interest for their separation are summarized in Figure 19. Bismuth can be separated by extracting it from a buffered solution at pH 2.6



19. Extraction coefficients of bismuth, lead and thallium as functions of pH and dithizone concentration in carbon tetrachloride. From E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience Publishers Inc., New York (1959), p. 557.

to 3.0 into 0.01% dithizone in chloroform as has been done by Rudenko for separation of carrier-free ThB(Pb^{212}) from ThC(Bi^{212}). It is expected that there will be some loss of lead in 0.01% dithizone. The lead recovery can be improved by shaking the last chloroform extract with 0.01 N acid. A similar separa-

tion has been made by Bambach and Burkey at pH 3.4 (B3) into dithizone-chloroform and by Fischer and Leopoldi at pH 2.8-3.0 (F7) into dithizone-carbon tetrachloride.

The method of extracting both the bismuth and lead together from basic cyanide solution and then removing the lead by shaking with dilute acid has been used in the separation of lead from monazite (P2) and from bismuth-lead mixtures by Moore (M5). The lead is normally removed into 0.01 N nitric acid solution. Bouissieres and Ferradini have investigated the purification of RaD(Pb^{210}), Ra(Bi^{210}) and Po mixtures by dithizone extraction (B4). Their results show that either of the above methods can be used effectively. They also note that Polonium behaves similarly to bismuth and can be extracted from acid solutions.

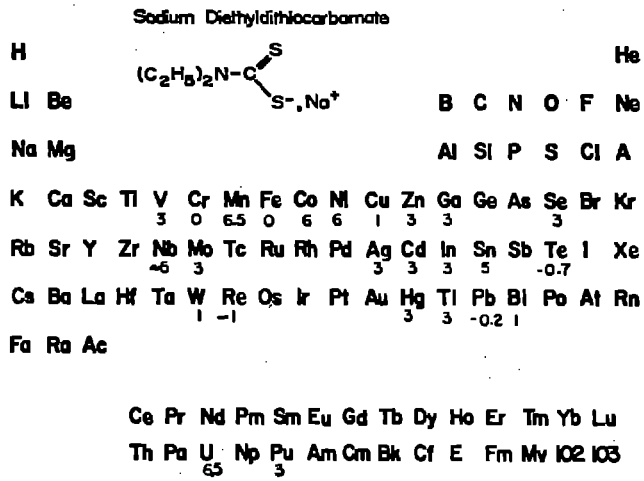
Separation from thallium can be accomplished tolerably well by fractional extraction. For example, using the extraction coefficients shown in Figure 19 it can be shown that if a solution of pH 4.0 containing 1 γ lead and 500 γ thallium is extracted twice with an equal volume of 0.01% dithizone in carbon tetrachloride, and the combined extracts are shaken twice with pH 5.0 buffer solution, .9997 γ of lead and .0002 γ of thallium should remain in the organic phase (S5). Perhaps a preferred method is to effect a separate lead-thallium separation by a selective precipitation of lead on strontium sulfate or by extracting the lead into carbamate reagent from 1.5 M hydrochloric acid solution (see below).

Diethyldithiocarbamate

The most commonly diethyldithiocarbamate salt used is the sodium salt which is a white-crystalline compound, readily soluble in water, less soluble in alcohol. The reagent is generally used in a 1-2% aqueous solution. A certain similarity between the extractability of metals as diethyldithiocarbamates

and dithizones is evident. Diethyldithiocarbamic acid reacts with a greater number of elements and this fact, together with the more limited pH range of extraction of its complexes, makes it less generally useful than dithizone for determination and separation of metals. The principle use of this reagent in lead separations stems from its utility in separating lead from elements which extract with lead dithizonate in basic solution (bismuth and thallium) and in separating lead from solutions containing calcium or magnesium together with phosphorus, a combination which precludes dithizone extraction from basic solution.

Figure 20 taken from the review of Freiser and Morrison (F1) shows the elements extractable in sodium diethyldithiocarbamate solution and the pH at which each can be completely extracted. A variety of solvents were used for the extractions indicated in Figure 20. The solvents used for lead were ethyl ether or ethyl acetate (M1).



20. Elements extractable with sodium diethyldithiocarbamate. The number under an element symbol indicates the pH value at which the element can be completely extracted. From H. Freiser and G. H. Morrison, "Solvent Extraction in Radiochemical Separations", Ann. Rev. Nuc. Science 9, 221 (1959).

Milner, Edwards and Paddon have tested a large variety of solvents for diethyldithiocarbamate extraction of lead and report that trichloroethylene or tetrachloroethane are superior (M12). They found that lead extracts quantitatively over the pH range 0.5 to 4.5 from a 0.1 to 1 M nitric or perchloric acid solution. The organic phase was 1 per cent diethyldithiocarbamate in trichloroethylene. They extracted lead under these conditions to effect a separation from thorium which does not extract (M12). A similar separation from thorium has been used by Gorsuch (G4) in which he extracts lead diethyldithiocarbamate into isoamyl acetate from pH 3.0-3.2 nitrate solution leaving the thorium in the aqueous phase.

Investigation of the diethylammonium diethyldithiocarbamate-chloroform extraction has shown that lead can be quantitatively extracted from 1.5-2.0 M hydrochloric acid solutions (M14). From 5.3-6 M hydrochloric acid solutions it is not extracted (S13). Lead is also not extracted into diethylammonium dithiocarbamate-carbon tetrachloride from 12 M hydrochloric acid (T3). A convenient separation of lead from bismuth and thallium is to extract the lead with the chloroform reagent from 1.5 M hydrochloric acid leaving bismuth and thallium in the aqueous phase. Elements extracting to a greater or lesser extent from 1.5 M hydrochloric acid include zinc, cadmium, tin (IV), indium, and platinum (IV) (S5). Elements other than bismuth and thallium not extracted from 1.5 M acid are manganese, vanadium (V), Cerium-III, uranium-VI, antimony-V, chromium-III, zirconium, titanium and aluminum (S5). The bismuth can subsequently be extracted from 6 M hydrochloric acid (S13). An alternative method for separating lead and bismuth is to extract them together into carbon tetrachloride after treatment with sodium diethyldithiocarbamate from a tartarate, citrate, cyanide solution at pH 12. Lead and bismuth are removed from the organic phase by shaking with 12 M hydrochloric acid and bismuth is then

extracted from the hydrochloric acid solution with diethylammonium dithiocarbamate-carbon tetrachloride reagent leaving lead in the aqueous phase. This procedure suffices to separate lead from alloys and a wide range of complex mixtures (T3). Diethylammonium diethyldithiocarbamate-carbon tetrachloride reagent can be prepared by the following procedure: dilute 3 ml diethylamine with 7 ml carbon tetrachloride and place in a brown-stoppered bottle. Mix 1 ml carbon disulfide and 9 ml carbon tetrachloride and add 4-5 ml of this mixture to the bottle and shake. Cool and add remainder of the disulfide solution (L7). The reagent keeps one week. On day of use, dilute 1:9 with carbon tetrachloride.

Another procedure for separation of lead from bismuth and thallium utilizes extraction of lead diethyldithiocarbamate from a citrate solution of pH 7 by a mixture of amyl alcohol and toluene (equal volumes). Lead is returned to the aqueous phase by shaking with 0.5 M hydrochloric acid. Bismuth and thallium are stated to remain in the organic phase (S5).

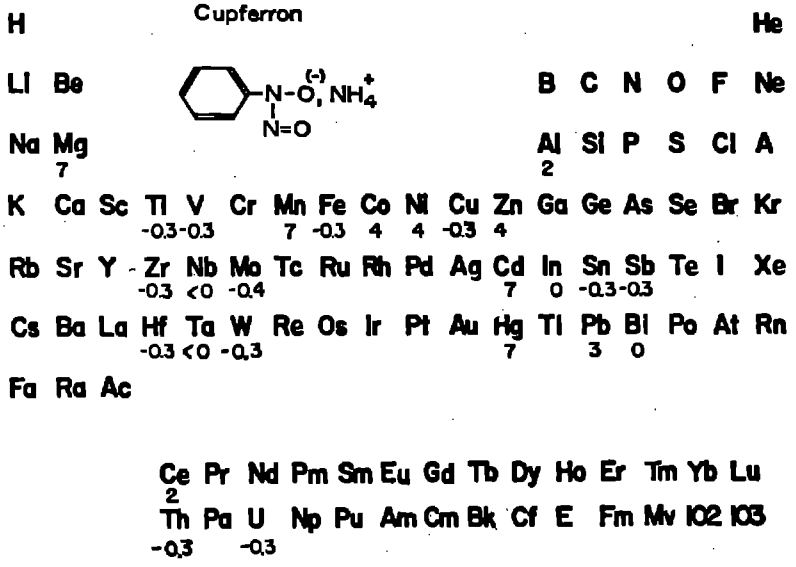
Chernikov and Dobkna have reported that lead diethyldithiocarbamate can be extracted from fluoride solutions by ethyl acetate or chloroform at pH 0.3 (C4). This can be used as a separation from zinc which is extracted at pH 3.

After extraction of the lead diethyldiothiocarbamate into an organic solvent the lead can be removed by shaking with concentrated hydrochloric acid (T3), or the organic solvent evaporated and the residue dissolved in hydrochloric acid (G4) followed by colorimetric determination as the dithizonate or by some other means. Alternatively, the lead can be determined colorimetrically in diethyldithiocarbamate-carbon tetrachloride solution by shaking with excess copper sulfate solution to convert the lead complex into the copper complex which is determined at 435 mu (T3). Lead complexed with diethylammonium diethyldithiocarbamate is usually removed by evaporating the

organic solvent and destroying the organic residue with sulfuric acid-perchloric acid (L7) or with sulfuric acid-nitric acid (M14).

Cupferron

Frieser and Morrison indicate that the cupferron-lead complex can be extracted at pH 3 (F1). The solvent is probably isoamyl alcohol. Details of the extraction are not given but some useful separations appear possible. Figure 21 shows the pH at which the cupferrates of a number of elements can be extracted.



21: Elements extractable by cupferron. The number under an element symbol indicates the pH value at which the element can be completely extracted. From H. Freiser and G. H. Morrison, "Solvent Extraction in Radiochemical Separations", Ann. Rev. Nuc. Science 9, 221 (1959).

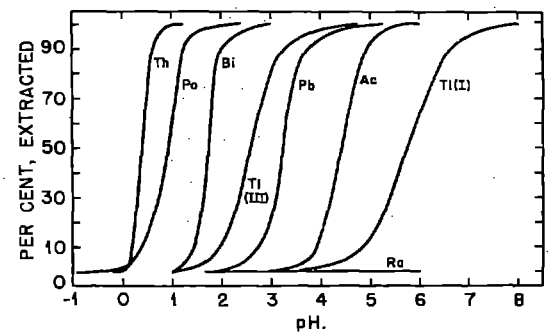
8-Hydroxyquinoline (Oxine)

Most metal 8-hydroxyquinolates are soluble in chloroform and can be extracted from aqueous solutions by the use of this solvent (S5). Exceptions are calcium, magnesium, tungsten, silver and gold. As noted in section IV-4A precipitation of the

lead complex from aqueous solution is complete in the pH range 8.5 to 12.3. This is also the pH range of optimum extraction (M1). Insofar as precipitation separations are possible by suitable pH adjustments, extraction separations are in general feasible. Greater selectivity of extraction can probably be realized by the use of complexing agents but these have not been investigated for lead.

2-Thenoyltrifluoroacetone (TTA)

TTA extractions have been used for separation of many metal ions. This reagent has not been widely used in lead separations largely because of the popularity of dithizone and dithiocarbamate extractions. TTA was designed expressly to permit extraction from stronger acid solutions than other chelating agents. Thus many ions can be extracted without interference from hydrolysis. Problems due to the instability of some chelates such as the diethyldithiocarbamates in mineral acids are also avoided in TTA extractions. In addition, the high power dependence of the extraction on acidity makes the separation of one metal ion from another very sharp. Typical extraction curves for lead and a number of other ions are shown in Figure 22 (H11). It is apparent from this figure that lead can be effectively separated



22. Extraction of tracer quantities of thorium, polonium, bismuth, lead, thallium, radium and actinium from aqueous solution by an equal volume of 0.25 M thenoyltrifluoracetone (TTA) in benzene. From F. Hagemann, J. Am. Chem. Soc. 72, 768 (1952).

from thorium, polonium, bismuth, radium, actinium and thallium by careful control of the pH of the aqueous solution. The thallium separation is facilitated by addition of a reducing agent such as hydroxylamine hydrochloride to keep thallium in the univalent state. It is of interest to note that the elements shown in Figure 22 are those most often present in naturally radioactive or in cyclotron produced sources of lead radioisotopes.

A comprehensive review of TTA extraction by Poskanzer and Foreman has recently appeared which summarizes known extraction coefficients (P4). The pH values corresponding to 50% extraction into 0.2 M TTA dissolved in benzene are shown in Figure 23. Using these values and the curves of per cent extraction vs. $pH-pH_{50}$ shown in Figure 24 the optimum pH for separation of two or more elements can be determined (P4). In In most cases the value of X to be used in Figure 24 should be the oxidation state of the species extracted. The values of X to be used for exceptions to this rule are shown in parenthesis in Figure 23. $pH-pH_{50}$ represents the variation of the pH of the aqueous phase from the pH for 50 per cent extraction.

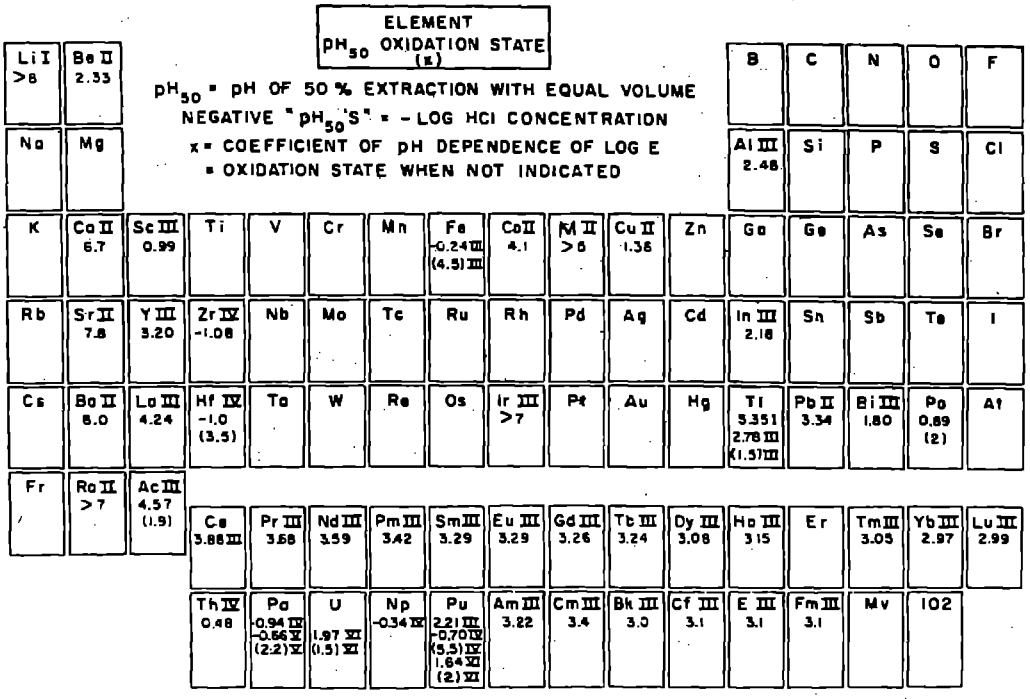
Acetylacetone

Acetylacetone can be used as both solvent and complexing agent in extraction of numerous metal ions. Lead extracts completely at pH 7.4 (F1). Lead has been separated from copper, uranium and bismuth by extraction at pH 7.4 (K9) from chloride solutions. Copper and uranium are both extracted at pH 2.3-5 and bismuth comes out of solution as the oxychloride above pH 1 and does not extract. Extraction of lead acetylacetonate into chloroform or butyl acetate is incomplete and is not useful for lead separations (T4).

8-Hydroxyquinaldine

Hynek has reported the separation of lead from alloys

EXTRACTION OF THE ELEMENTS WITH 0.2M TTA IN BENZENE

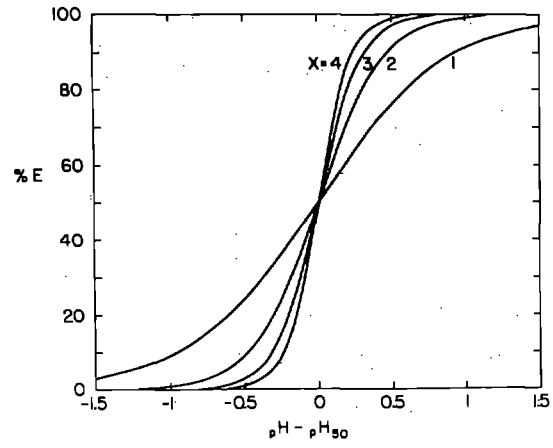


23. Elements extractable in thenoyltrifluoracetone. The numbers under an element symbol is the pH at which 50 per cent of the element is extracted into an equal volume of 0.25 M TTA in benzene. The figures in parentheses give a value of X to be used with Figure 24 to get pH dependence of extraction. When no value is given, the oxidation state of the element is to be used. From A. M. Poskanzer and B. M. Foreman, Jr., J. Inorg. and Nuc. Chem. 16, 323 (1961).

by extraction with 8-hydroxyquinaldine from an alkaline, cyanide-hydrogen peroxide medium (H12). After an intervening extraction at pH 5 to eliminate traces of impurities which would coextract with lead, the lead complex was extracted at pH 9 and determined spectrophotometrically in the organic phase.

C. Amalgam exchange.

Devoe, Kim and Meinke have described a fast and selective separation based on the rapid exchange of elements



24. Extractability vs. pH-pH_{50} for elements shown in Figure 23. The pH_{50} values should be taken from Figure 23 and the value of X to be used should be the oxidation state of the element or in some cases the value shown in parentheses in Figure 23. From A. M. Poskanzer and B. M. Foreman, Jr., J. Inorg. and Nuc. Chem. 16, 323 (1961).

present in a dilute amalgam and its ions in solution (D1). The yield of this process decreases as the amount of the element in the aqueous phase increases relative to the amount in the amalgam. It also decreases in the presence of oxidizing agents ($M_nO_4^-$, $Cr_2O_7^=$, etc.). For five-minute stirring of a 2 per cent amalgam with a volume ratio for aqueous phase to amalgam of 40:1, 90 per cent of the carrier-free lead-212 was removed from a 0.5 M sodium nitrate solution. Presumably the lead could be removed from the amalgam by shaking with an aqueous solution of a suitable oxidizing agent.

8. Ion exchange.

The speed, convenience and selectivity of ion exchange separations have gone far toward making this the separation method preferred by radiochemists. Ion exchange is most useful for final purification of a radioelement or for separation from a few interferring species. Specific separations from general mixtures are usually less successful. This is not a serious

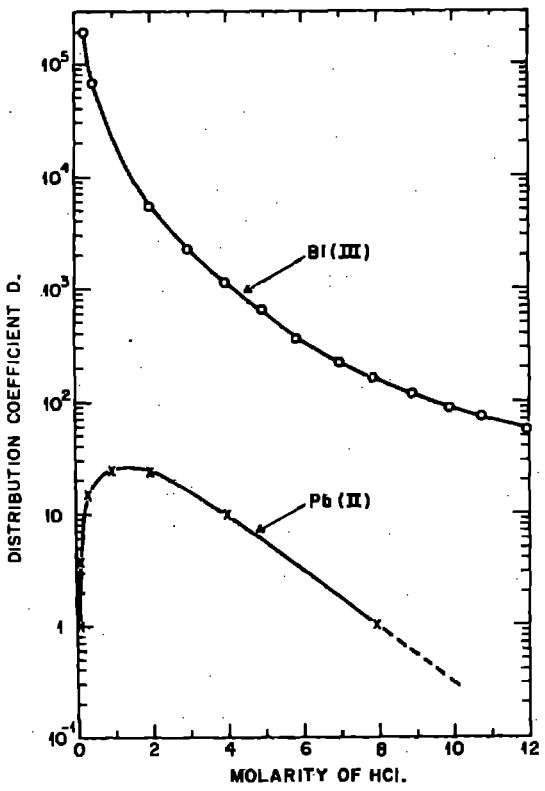
failing because often only a few radioelements are present in the sample or preliminary group separations can be carried out rapidly and quantitatively by precipitation reactions, solvent extraction or electrodeposition. Macroquantities of impurity often impairs ion exchange separations by resin-loading effects even if the impurity is not strongly absorbed on the resin. In general, separations are more complete if the amount of carrier is minimized but up to 10-20 mg of inert carrier of the element of interest can often be tolerated by increasing the amount of resin in the column.

A. Anion exchange.

From Hydrochloric Acid

The adsorption of lead (and bismuth) on a strong base quaternary amine anion-exchange resin in hydrochloric acid solution has been investigated in detail by Nelson and Kraus (N2). The resin used in this work was Dowex-1, 200-230 mesh. It was found that the absorbability of lead-II was low in dilute hydrochloric acid (D = 1 in 0.05 M HCl) and increased at first with increasing hydrochloric acid concentration. Adsorption reached a maximum (D = 25) near 1.5 M hydrochloric acid and then decreased rapidly. Negligible adsorption (D < 1) occurred above 8 M hydrochloric acid. The distribution coefficients obtained for lead and bismuth as a function of the hydrochloric acid concentration are shown in Figure 25. The adsorption of lead, although relatively small at its maximum, is sufficient to permit its separation from most elements in the periodic table. Distribution coefficients for adsorption of large number of elements on Dowex-1 resin as a function of the hydrochloric acid concentration are shown in Figure 26. This figure is taken from the review article of Kraus and Nelson (K7). A few examples of lead separations are shown on curves A, B and D of Figure 27 (N2). It is of interest to note that by altering the conditions

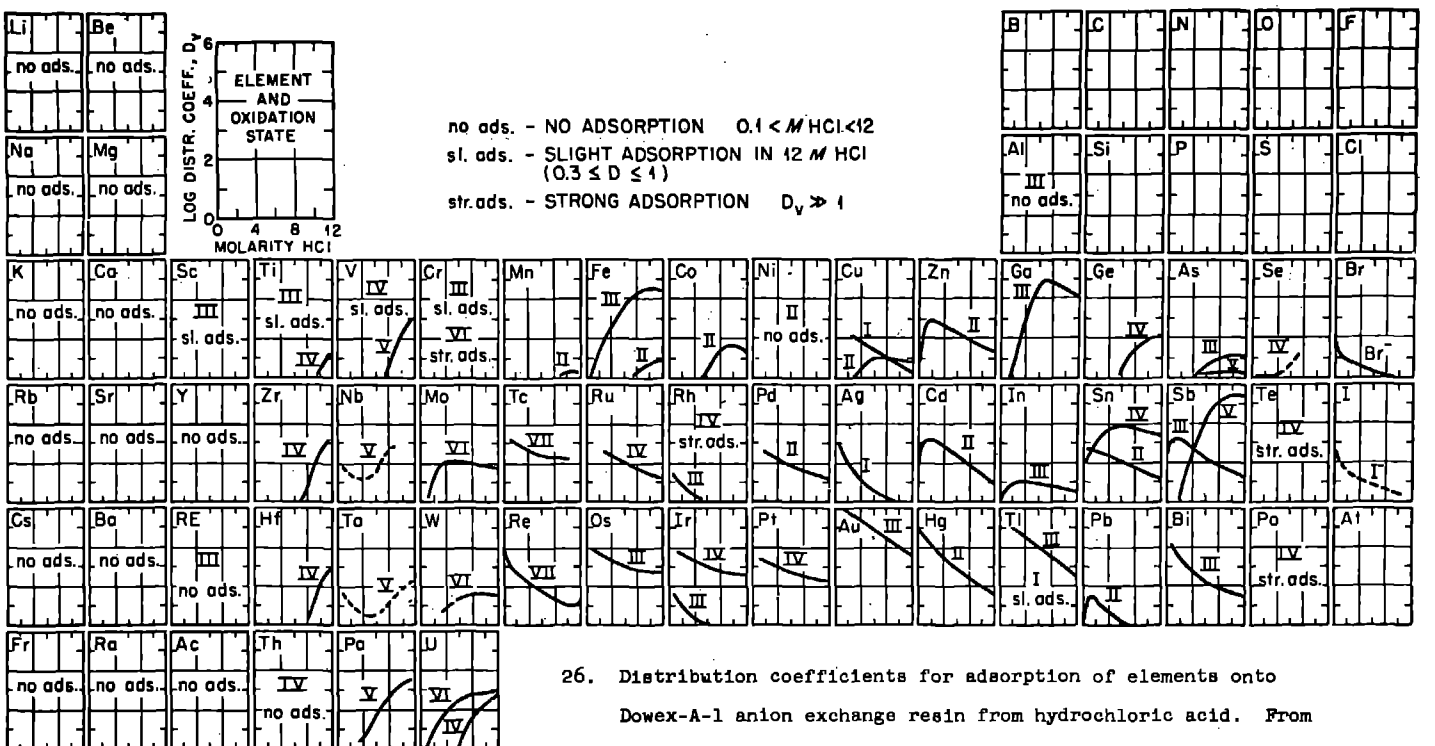
it is possible in some cases to change the order of elution as shown for lead and iron-III in curves A and B of Figure 27. Lead, bismuth and polonium have been separated from radium solutions by Dowex-1 anion-exchange columns (H6)(H10)(P3) by putting the mixture onto the resin in 1-2 M hydrochloric acid. The radium passed



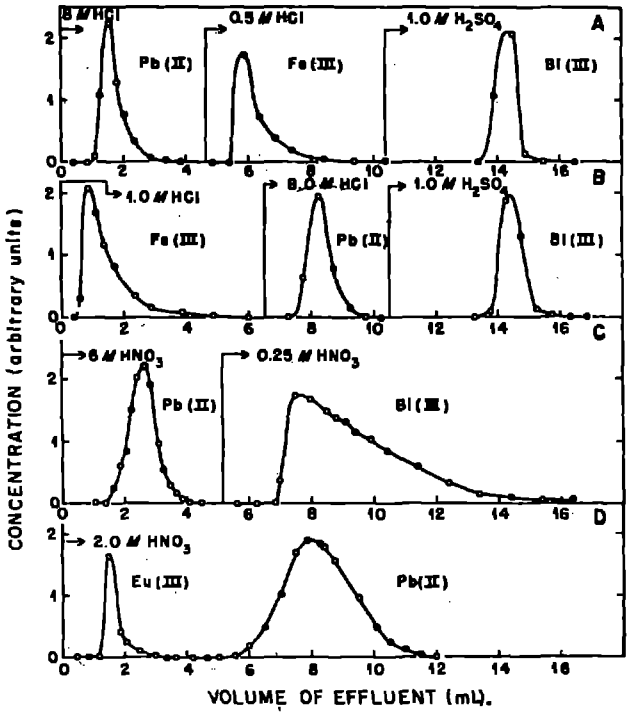
25. Distribution coefficient vs. hydrochloric acid concentration for adsorption of lead and bismuth on Dowex-A-1 anion exchange resin from hydrochloric acid solution. From F. Nelson and K. A. Kraus, J. Am. Chem. Soc. 76, 5916 (1954).

directly through the column and the lead was removed after about 5 column volumes of eluant had been passed through. The bismuth was subsequently removed with concentrated hydrochloric acid and the polonium with concentrated nitric acid (H6).

The speed possible in ion exchange separations make this a uniquely favorable separation method for many applications.



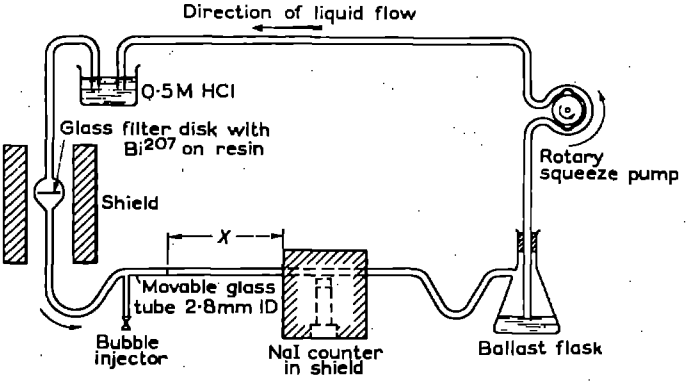
26. Distribution coefficients for adsorption of elements onto Dowex-A-1 anion exchange resin from hydrochloric acid. From K. A. Kraus and F. Nelson, Proc. of the First U.N. Conf. on Peaceful Uses of At. Energy 7, 113 (1955).



27. Separations involving PbII in hydrochloric acid and nitric acid solutions (0.30 sq. cm. columns, length A, 4.7 cm; B, 4.7 cm; C, 6.8 cm; D, 12.2 cm, 200-300 mesh Dowex-1, flow rate, 0.5 cm/min). From F. Nelson and K. A. Kraus, J. Am. Chem. Soc. 76, 5916 (1954).

Anion exchange separations have been used for example to separate lead isotopes of a few seconds half life from bismuth parent activities (S9). The column was maintained at 82.3°C by refluxing isopropyl alcohol through an external jacket in order to increase the rate of equilibration. Bismuth was adsorbed on the resin and lead was eluted. Lead daughters of half life down to one or two seconds could then be removed from the resin rapidly enough with very dilute hydrochloric acid to allow their lifetimes and radiation characteristics to be measured. A similar method has been used by Campbell and Nelson to make measurements of the characteristics of 0.8 sec lead-207M produced from decay of bismuth-207 (C3). In this work 200 mesh Dowex-1 (10% cross linked) resin was used at room temperature. These workers have utilized a flow

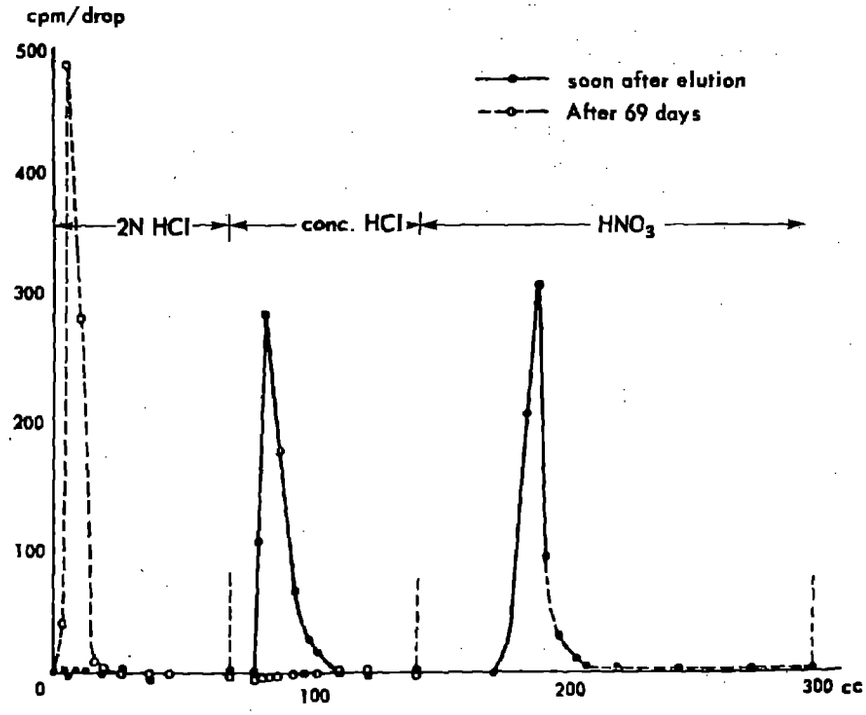
technique in which the solution is passed through the resin bed past on injector which injects bubbles used to measure the flow rate and then directly to a scintillation counter. By varying the spacing between the detector and the resin the half life of lead-207M was measured as 0.84 ± 0.02 sec (C3). The flow apparatus is shown in Figure 28. The method could be extended (in favorable cases) to measurements of isotopes of half lifes of the order of milliseconds.



28. Schematic diagram of flow apparatus for measurement of Pb^{207m} half-life. From E. C. Campbell and F. Nelson, J. Inorg. and Nuc. Chem. 3, 233 (1956).

Similar results have been obtained using other strong base quaternary anion resins in hydrochloric acid solution. Jentzsch and Frotscheu have reviewed the use of Wolfatit L-150 anion exchange resin (J1). Table XVIII shows the hydrochloric acid concentration at which a number of elements are eluted from Wolftit L-150. Amberlite XE-98 (65-120 mesh) resin was used by Ishimori for separation of Pb^{210}(RaD), Bi^{210}(RaE) and Po^{210}(RaF) (I5). The resin was packed in a 3 cm by 0.85 cm diameter column. After converting the resin to the chloride form by treatment with concentrated hydrochloric acid the elution curves shown in Figure 29 were obtained.

Russian workers have successfully separated small amounts of lead from bismuth, cobalt, nickel, iron and copper



29. Elution sequence for RaD (Pb^{210}), RaE (Bi^{210}) and RaF (Po^{210}) on Amberlite X98 anion exchange resin. From T. Ishimori, Bull. Chem. Soc. Japan 28, 432 (1955).

by using AN-2F and TM anion exchange resin (S10). The mixtures were loaded on the resin in 8 M hydrochloric acid. The cobalt, copper and iron were desorbed with 4 to 0.05 M hydrochloric acid, the lead with 0.02 M hydrochloric acid and the bismuth with 1 M sulfuric acid (S10).

The behavior of lead on De-acidite FF anion exchange resin (40-60 mesh) has been investigated by Milner, Edwards and Paddon (M12). They find the behavior to be similar to that noted above for Dowex-1. The adsorption is strongest from 2 M hydrochloric acid but lead began eluting at this concentration after a few column volumes of eluant had passed through. Gorsuch used De-acidite FF (100-200 mesh) to separate lead from thorium (G4)(G5). After loading the thorium solution onto a 10 cm x 1.5 cm diameter column in 2 M hydrochloric acid and washing the thorium

Table XVIII
Elution of metal ions from Wolftit L-150 anion exchange resin with hydrochloric acid.

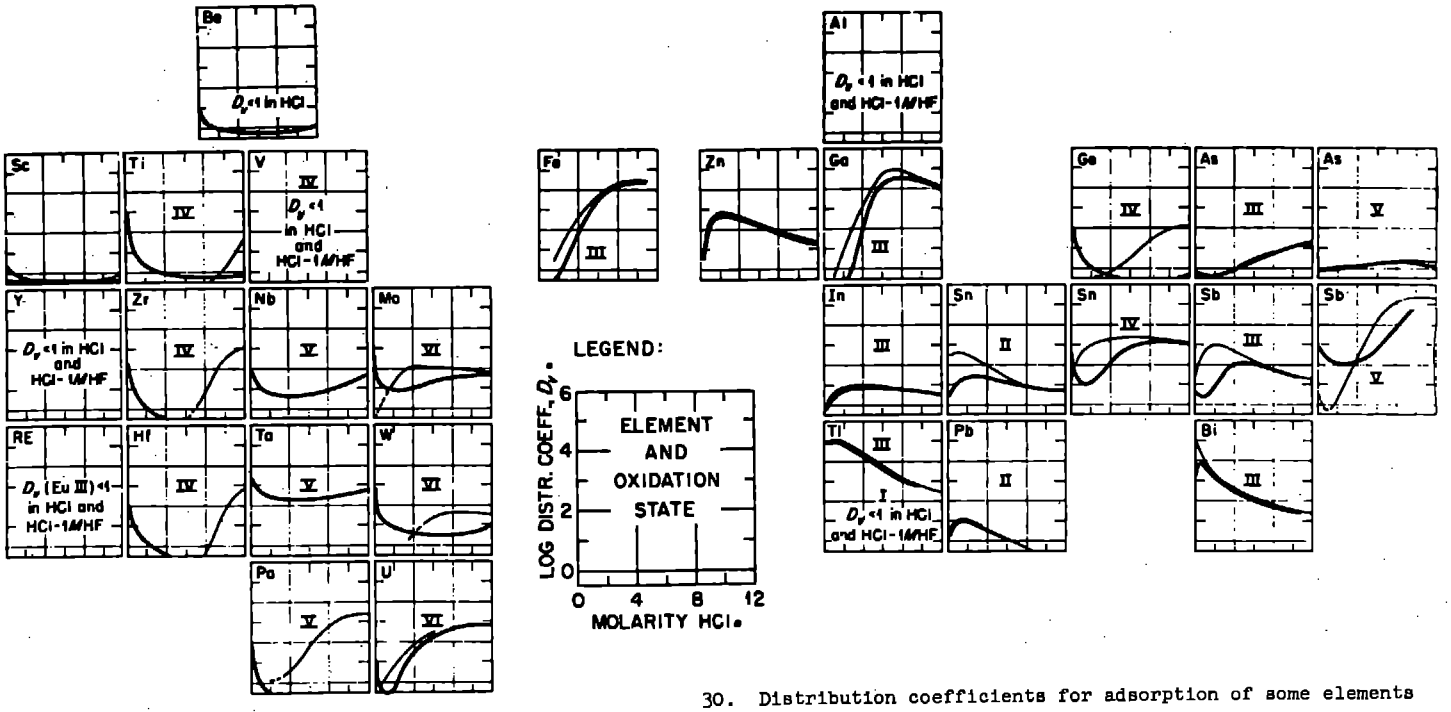
Element	Hydrochloric Acid Concentration (Molarity)										
	12.5	11-10	7.5	6.5	5	4	1.5	1.0	0.5	0.05	0.005
Al	X										
Mg	X										
Li	X										
Na	X										
K	X										
As III		X									
Ca		X									
Ni		X									
Fe II			X								
Co				X							
Mn II				X							
Fe III					X						
Cu						X					
Sn IV							X				
In								X			
Zn									X		
Cd										X	
Pb											X

From ref. (J1).

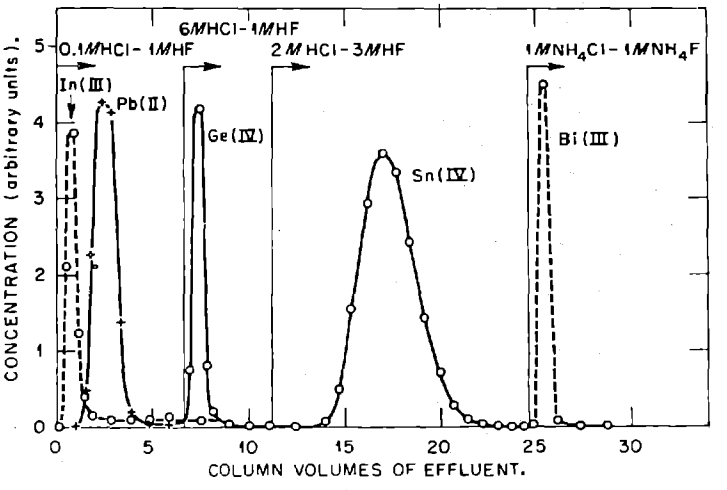
through the resin bed with 2 M hydrochloric acid, the lead was eluted in a sharp band with distilled water.

From Other Halic Acids

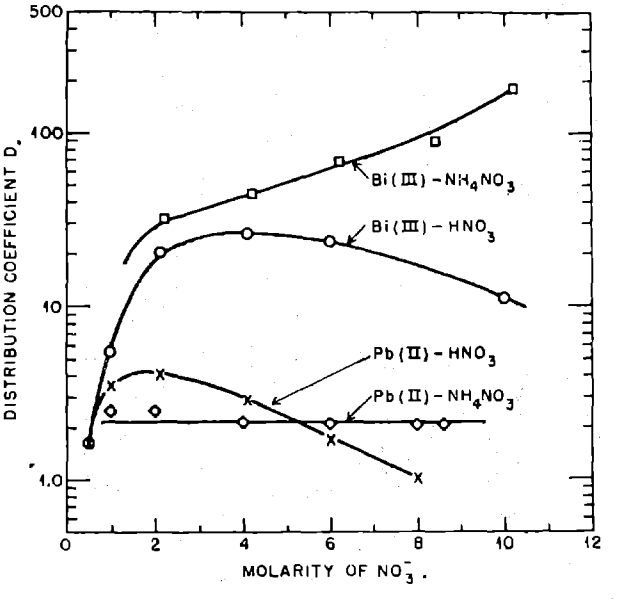
Hydrochloric acid-hydrofluoric acid mixtures are useful eluents in many anion-exchange separation procedures. The distribution coefficients for a number of elements on Dowex-1 resin from 1 M hydrofluoric- (0.01-12 M) hydrochloric acid solutions are shown in Figure 30 (from reference N4). Although the adsorption behavior of lead is relatively uneffected by the presence of the hydrofluoric acid, a number of elements such as tin-II, germanium-II, and titanium-IV, which behave much like lead in hydrochloric acid solution exhibit sufficiently different behavior in the mixture to make their separation from lead straightforward. An example of lead separations using mixed hydrochloric acid-hydrofluoric acid elements is shown in Figure 31. Faris has found that lead is only slightly adsorbed on Dowex-1 resin from hydrofluoric acid solutions



30. Distribution coefficients for adsorption of some elements on Dowex-1 anion exchange resin from hydrochloric acid-hydrofluoric acid solutions. The light lines show the adsorption behavior in 1 M HF solutions (except Zr(IV), Hf(IV), Nb(V), Ta(V) and Pa(V) where M HF = 0.5) as a function of hydrochloric acid concentration. The dark curves show the behavior in the absence of hydrofluoric acid. From F. Nelson, R. M. Rush and K. A. Kraus, J. Am. Chem. Soc. 82, 339 (1960).



31. A separation involving lead adsorbed on Dowex-1 anion exchange resin using HCl-HF eluent. From F. Nelson, R. M. Rush and K. A. Kraus, J. Am. Chem. Soc. 82, 339 (1960).



32. Distribution coefficients for adsorption of lead (II) and bismuth (III) onto Dowex-1 anion exchange resin from nitrate solutions. From F. Nelson and K. A. Kraus, J. Am. Chem. Soc. 76, 5916 (1954).

ranging in concentration from 1 M to 24 M (F8). Lead can be easily separated from Mo IV, Te IV, Sb V, Sn IV, Zr IV, Nb V, Pd II and As V with 5 M HF (F8).

Lead has been found to adsorb more strongly onto De-acidite FF anion exchange resin from 2 M hydrobromic acid solution than from 2 M hydrochloric acid solution (M12). Hydrobromic acid eluant has been used to separate lead from thorium (M12).

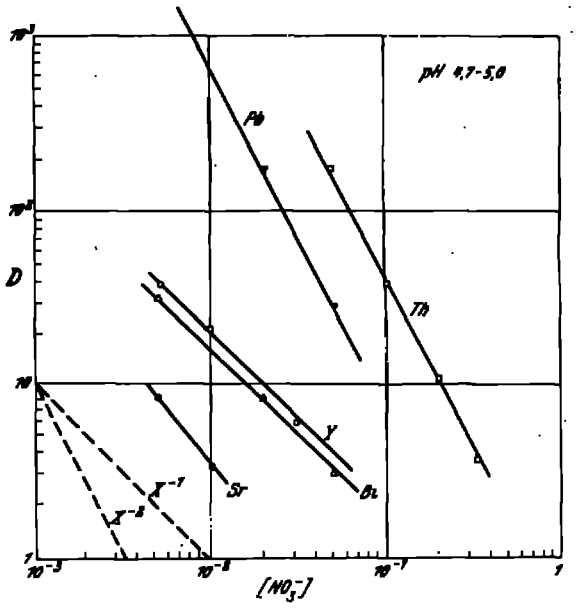
From Other Electrolytes

The distribution coefficients for lead (and bismuth) on Dowex-1 from nitrate solutions are shown in Figure 32 (N2). Lead is only very weakly adsorbed at all concentrations as might be expected from the failure of lead to form negatively charged nitrate complexes. Some useful lead separations using a nitrate system are possible as shown in curve C of Figure 27. In general, however, the same separations can be carried out as well or better with a hydrochloric acid system.

It is possible to adsorb lead onto anion exchange column by first loading the resin with iodide ion (K2), sulfide ion (K2) or phosphate ion (R4).

Influence of EDTA

The adsorption behavior of lead on anion exchange resins is drastically altered in the presence of EDTA. In contrast to the low adsorption of lead from nitrate solutions in the absence of EDTA is its strong adsorption in the presence of EDTA. The distribution coefficients of lead and a number of other elements onto Dowex-1 from nitrate solutions of varying nitrate composition in the presence of very dilute EDTA are shown in Figure 33 (S11). The EDTA is present in excess over the radioelements in order to convert them to their EDTA complexes but the amount is still small compared with the concentration of nitrate ions so the ion exchange resin is almost completely in the nitrate form.



33. Distribution coefficients of radioelements between nitrate-loaded Dowex-1 and nitrate solutions, both containing some EDTA, at pH 4.7-5.0. From T. Schönfeld, M. Wald and M. Brund, Proceedings of the 2nd U.N. Conference on the Peaceful Uses of At. Energy 28, 48 (1958).

The significant process is then exchange of nitrate anions in the resin phase with complex anions containing the radioelement:

$$n(R^+)NO_3^- + Mc\ Y^{n-} \rightleftharpoons (R^+)n\ Mc\ Y^{n-} + n\ NO_3^-$$

If more concentrated solutions of the EDTA are used, (as the disodium salt, represented as Na_2HaY) then the resin is in the form of the anionic complexon and the process of interest is:

$$n(R^+)_2H_2Y_2^- + MeY^{n-} \rightleftharpoons 2(R^+)_n\ MeY^{n-} + nH_2Y^{2-}$$

The distribution coefficients of the same radioelements of Figure 33 on Dowex-1 resin loaded with EDTA as a function of the EDTA concentration of the eluant is shown in Figure 34.

It is also useful to consider the effect of varying the pH of the solution since the stability of the various EDTA complexes is known to be pH sensitive. The effect on the distribution coefficient for lead between nitrate loaded Dowex-1 and nitrate solution containing dilute EDTA is shown in Figure 35.

In these systems the slope of the distribution coefficient curve is primarily dependent on the charge on the anionic metal complex ion. The slopes for singly and doubly negative ions are shown by the dotted lines in Figures 33, 34 and 35. A number of useful separations are suggested by the distribution coefficients of Figures 33-35. It is especially notable that the order of elution of lead and bismuth under most conditions is the reverse

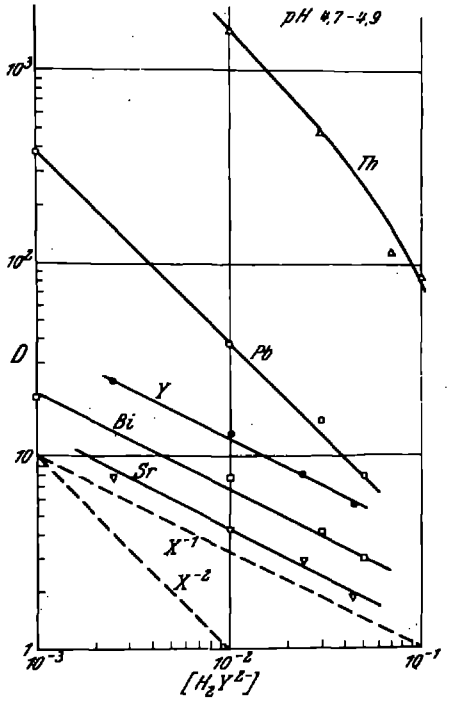


Figure 34

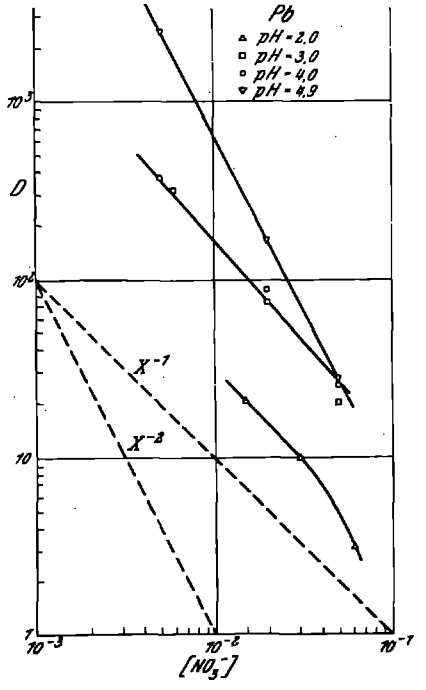


Figure 35

34. Distribution coefficients of radioelements between Dowex-1 loaded with EDTA and solutions of EDTA (pH = 4.7-4.9). From T. Schönfeld, M. Wald and M. Brund, Proceedings of the 2nd U.N. Conference on the Peaceful Uses of At. Energy 28, 48 (1958).

35. Distribution coefficients of lead (Pb^{210}) between nitrate-loaded Dowex-1 anion exchange resin and nitrate solutions, both containing some EDTA for different pH values. From T. Schönfeld, M. Wald and M. Brund, Proceedings of the 2nd U.N. Conference on the Peaceful Uses of At. Energy 28, 48 (1958).

of that normally encountered, with the lead being the more strongly adsorbed in the presence of EDTA. This can be used, for example, to elute bismuth daughter activities from adsorbed lead isotopes. It is apparent that a study of the pH dependence of adsorption for a larger number of elements should lead to many selective and quantitative separation procedures.

B. Cation exchange.

Bonner and Smith have studied the relative adsorption of a large number of metal ions on Dowex-50 from perchlorate solutions (B5). Table XIX summarizes their results. Although the order and degree of adsorption is affected by the presence of complexing agents such as chloride ion the selectivity scale shown in Table XIX indicates that Dowex-50 is probably best used for group separations.

Table XIX
Relative adsorption of metal ions on Dowex-50 from perchloric acid solutions.

Metal Ion	Per Cent Cross-Linkage 4%	8%	12%
Li^+	1.00	1.00	1.00
H^+	1.32	1.27	1.47
Na^+	1.58	1.98	2.37
NH_4^+	1.90	2.55	3.34
K^+	2.27	2.90	4.50
Rb^+	2.46	3.16	4.62
Cs^+	2.67	3.25	4.66
Ag^+	4.73	8.15	22.9
Tl^+	6.71	12.4	28.5
VO_2^{++}	2.36	2.45	3.34
Mg^{++}	2.95	3.29	3.51
Zn^{++}	3.13	3.47	3.78
Co^{++}	3.23	3.74	3.81
Cn^{++}	3.29	3.85	4.46
Cd^{++}	3.37	3.88	4.95
Ni^{++}	3.45	3.93	4.06
Ca^{++}	4.15	5.16	7.27
Sr^{++}	4.70	6.51	10.1
Pb^{++}	6.56	9.91	18.0
Ba^{++}	7.47	11.5	20.8

From ref. (B5).

Fritz and Karraker have recently reported the use of ethylene diammonium perchlorate solution to effect group

separations on 100-200 mesh, 8% cross-linked Dowex-50 (F9). Most divalent cations with the exception of barium-II and lead-II are eluted from the column with 0.1 M eluent. The trivalent cations with the exception of bismuth-III are then removed with 0.5 M eluent. Lead and barium are removed with this fraction. Bismuth, thorium and zirconium remain quantitatively on the column after this treatment. This method has been used for specific separations of lead from thorium-IV and from bismuth-III with the lead fraction being recovered in high purity and high yield (F9). Sequential group separations using a number of different complexing agents in conjunction with Dowex-50 resin has also been described by Blaedel, Olsen and Buchanan (B9). In this scheme lead is removed from the resin with 2 per cent citric acid at pH 3.0 along with sixteen other elements. The notable separations appear to be from copper, zinc, cadmium, strontium barium and thallium which adsorb on the resin in this medium.

Mercury, lead and bismuth have been separated on Dowex-50 with hydrochloric acid (T2). The ions were loaded in 0.1 M hydrochloric acid, mercury was eluted with 0.3 M bismuth with 0.6 M and lead with 6 M hydrochloric acid.

Minami and Ishimori (M13) have separated lead and barium by adsorbing the ions from nitrate solution onto Dowex-50 in the ammonium form and eluting the lead with ammonium acetate solution at pH 6.1. The barium remains on the resin and can be eluted with 10% ammonium chloride solution (M13).

An interesting method for preparation of carrier-free lead-212 (ThB) by the use of Dowex-50 resin has recently been described by Kahn and Langhorst (K8). The procedure involves refluxing a thorium nitrate solution in 1 M nitric acid 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, hydrogen form). The thoron 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 to polonium-216 which decays to lead-212. The lead-212 is washed onto and retained by the resin and can be removed subsequently with 1 M hydrochloric acid.

A number of other lead separations have been described in the recent review by Schindewolf (S12). These include separations from indium and antimony on Dowex-50 by loading in 0.1 M hydrochloric acid, removal of antimony with 0.2 M, indium with 0.4 M and finally lead with 1-2 M hydrochloric acid. Copper, zinc and iron-III are removed with the lead (S12). Separation of lead from molybdenum on Wolftit-F cation exchange resin by elution of molybdenum with citric acid is also described (S12).

As in the case with anion-exchange resins, the presence of EDTA or other organic complexing agents alter the adsorption behavior of lead on cation-exchange resins. For example the barium-EDTA complex is less stable than that of lead. By passing a mixture of the lead and barium EDTA complexes adjusted to pH 4-4.5 through Dowex-50 resin, only lead passes through, barium is adsorbed (W5). An EDTA solution of pH 10.5 can be used to remove barium from the resin.

9. Filter paper chromatography.

A. Introduction

The separation of inorganic metals by filter paper chromatography seems to be ideally suited for many radiochemical applications. This separation method usually works best with trace amounts of material; it is quantitative, convenient, does not require much attendance, does not involve complex equipment or solutions, adapts well to remote handling and can be fast. In addition, selective separations can be performed from complex mixtures. The resultant product can be easily concentrated or in some cases radioactivity measurements can be made on sections cut

or punched from the filter paper used in the separation. In spite of these advantages and the availability of reviews (L8) (S15) outlining the method, radiochemists have been slow to adopt or adapt this procedure to the separation of radioisotopes. The separation of radioactive mixtures adds the advantage that the radioactivity often provides a method of locating the fraction (or fractions) of interest with high sensitivity and speed.

Perhaps the voluminous amount of published data on chromatography has discouraged many radiochemists from utilizing the method. The simplicity of the technique tends to cause a rather emperical approach to be taken toward a specific separation and this has resulted in the publication of a confusing variety of conditions, solvents and results. The book by Lederer and Lederer (L8) has done much to clear the air but it is still difficult for the radiochemist to select the conditions and reagents best suited to a given separation. At the risk of adding to the confusion an attempt will be made to briefly review the general technique, to summarize the published data on separation of lead and to attempt to show by noting selected separations how this technique can be of use to the radiochemist. A brief summary of related techniques is also given.

B. Techniques.

In brief, the method is to evaporate a small volume of a solution of the mixture to be separated onto a spot on a filter paper strip or at the center of a filter paper circle. This spot is known as the origin. An alternate method is to place the mixture in small volume onto the top of a column packed with filter paper pulp. A complexing solution is then caused to flow across the origin and along the filter paper. The ions may then tend to move with the flowing solvent, the

magnitude of the tendency depending on the details of the ion-solvent-filter paper interaction. This tendency is often different for different elements so they become separated into bands along the filter paper. One need only provide therefore, a suitable filter paper, a source of the solvent and the means for its flow. It is also necessary to prevent evaporation of the solvent during the separation, this is done by saturating the chamber with solvent vapors.

The paper used is usually standard analytical grade filter paper in the form of strips 1-3 cm wide and 30-40 cm long or circles up to 10 cm diameter. Pollard, McOmie and Elbeith have tried using a variety of filter papers including Whatman No. 1, No. 54 and No. 541 and find no appreciable difference in the relative separations obtained (P5). A number of other papers have been used, including Muktell OB (C5), Eaton-Dikeman Grade-301 (W7), D'Arches No. 302 (L9), Whatman No. 41 (M15). The main difference in the papers seems to be the wettability which influences the rate of flow of solvent (highest for Eaton-Dikeman Grade-301).

It is sometimes necessary when working with traces of material, to purify the filter paper before use. Iron is the major contaminant. A number of methods of purifying the paper have been used: (1) downward flow of hydrochloric acid for six days followed by washing the paper free of chloride with distilled water (P1); (2) washing with 8-hydroxyquinoline in aqueous ethyl alcohol solution followed by thorough washing with aqueous ethanol and drying (P5); (3) downward percolation with 1 M nitric acid, 1 M acetic acid and water (S16). The latter method is probably preferred and has been used by Warren and Fink (W7).

The movement of the solvent along the paper is usually by capillary flow and the chamber used can take many forms. Apparatus for ascending or descending flow of the solvent on paper strips are shown schematically in Figures 36 and 37 (from ref. S17).

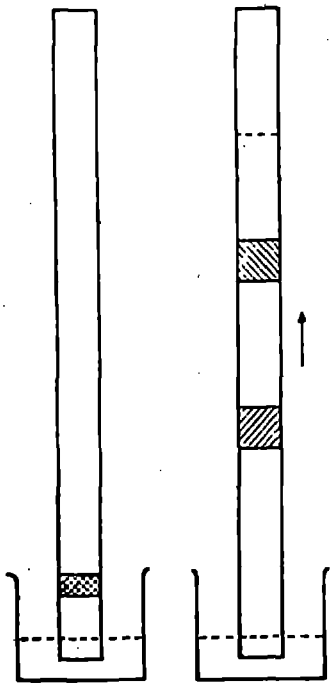


Figure 36

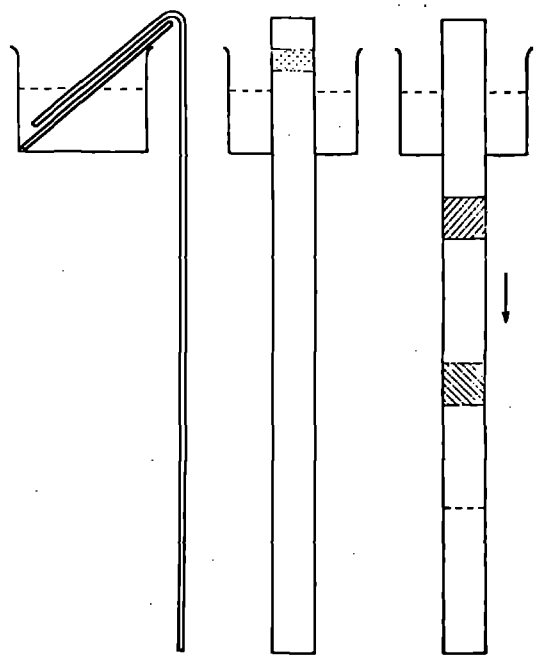


Figure 37

36. **Schematic description of chromatographic separations using upward migration of wash liquid. From H. H. Strain, Anal. Chem. 23, 25 (1951).**

37. **Schematic description of chromatographic separations using downward migration of wash liquid. From H. H. Strain, Anal. Chem. 23, 25 (1951).**

The enclosing chamber is usually a glass cylinder for separation on strips. If circular paper is used a simple chamber can be constructed from two evaporating dishes (L15). The solvent is placed in one dish over which is placed the circular paper with the edges of the paper extending over the rim of the evaporating dish. A tab (2-5 mm wide) is cut from the edge to the center of the paper and allowed to dip into the solvent to act as a wick. A second evaporating dish the same size as the first is then inverted over the filter paper to form an enclosed chamber.

After the separation is completed the paper is dried

and the bands located by colorimetric reactions (L8) or radioactivity (F10). The element can then be removed from the chromatogram by wet digestion of the filter paper or by leaching with acid. Lead can be removed quantitatively by boiling the paper with small quantities of 2 M nitric acid (P1).

C. Compilation of R_f values.

The relative separations obtained are indicated by the relative R_f values, for each component. The R_f values are defined by

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

The R_f values obtained are relatively independent of the rate of solvent flow or the distance the solvent front has moved from the origin. Good separations can usually be achieved only if the R_f values of adjacent bands differ by 0.1 unit or more. In some cases, where the bands are abnormally wide or where tailing of one or more components occurs, larger differences in the R_f values are required. It is customary to flow the solvent for about 20 cm in filter strip separations.

For equivalent conditions the R_f values for circular paper chromatography are generally larger than those for paper strip chromatography. The R_f values for circular paper using central feed are sometimes called R_{fc} values and have been found to be closely equivalent to the square root of the R_f values obtained with paper strips (L15)(S14).

As in the case of ion exchange, paper chromatography is most often used as a final separation from complex mixtures after rather general group separations have been performed. Table XX summarizes the published R_f values for lead and a number of other elements of particular interest in lead separations for a number of different solvents. Elements produced in charged particle or neutron irradiations in which lead radioisotopes are made have been included in Table XX. In addition

the other members of the so-called "copper group" and "tin group" of elements which form basic sulfides have been included to show the behavior of elements with chemistry similar to lead. R_f values for many other species are included in published tabulations but in the interest of space and clarity these have not been included in the table. Reference to the original literature is recommended for separations not included. Iron-III has also been included in Table XX because it is a common contaminant of natural or laboratory samples.

D. Examples of separations.

Many separations are indicated by the R_f tabulation in Table XX. The choice of solvent depends not only on the contaminants present but also on the time limitation imposed by the half-lives of the radioisotopes being separated. A few of the possible separations will be pointed out.

Of the various separations shown using butanol together with nitric or hydrochloric acid one of the best combinations appears to be butanol plus 6 N hydrochloric acid (D5). This is item 16 of Table XX. The lead is well separated from all elements listed except copper. Butanol in combination with hydrobromic acid (K10) (items 35-37) appears to be a useful solvent for lead separations. For most solvents studied, the lead fraction remains at or near the origin. If large amounts of the more mobile species are absent (quantities greater than ~0.1-0.5 mg tend to tail along the paper) then the immobility of lead can be used in its separation. Some of the solvents showing this type of separation are: butanol-HCNS (M15) (item 1), isopropanol + 10% 5 N HCl (L10) (item 12); isopropanol + nitric acid (L8) (item 25). The simplicity of the technique is shown by the use of commercial ethanol and hydrochloric acid to obtain good separation of lead, copper, bismuth and cadmium (L10) (item 11).

Mercury, copper, bismuth, cadmium and lead have been

TABLE XX

Summary of R_f Values for Common Contaminants of Lead Samples

	Fe^{+++}	Cu^{++}	As^{+++}	Ag^{+}	Cd^{++}	Sn^{++}	Sb^{+++}	Au^{+++}	Hg^{+}	Hg^{++}	Tl^{+}	Tl^{+++}	Pb^{++}	Bi^{+++}	Solvent Mixture	Ref
1.		1.00	0.54	1.00	1.00		0.96			1.00			0.0	0.96	Butanol-HCNS[a]	M15
2.	0.19	0.09		0.0	0.61		0.70T	0.82		0.79			0.0T	0.59	Butanol+1NHCl	L9
3.	0.74	0.13		0.0	0.23		0.70	1.00		0.36			0.04	0.09	Butanol+1NHCl; paper impreg. with 1NNaCl	L9
4.	0.20	0.13	0.42	0.18	0.13	0.73	0		0.23	0.23			0.11	0.15	Butanol+2NHNO_3 cont. 0.1% Dibenzoylmethane	P5
5.	0.95	0.22	0.43	0.10	0.05	0.58	0		0.24	0.31			0.03	0.02	Butanol+0.1NHNO_3 cont. 0.5% Benzoylacetone	P5
6.	0.43	0.12	0.43	0.15	0.12	0.82	0.02		0.43	0.43			0.09	0.23	Butanol+2NHNO_3 cont. 1% Acetylacetone	P5
7.	0.13	0.15	0.45	0.08	0.15	0.70	0		0.50	0.50			0.09	0.20	Butanol+1NHNO_3 cont. 5% Acetoacetic ester	P5
8.	0.14	0.17	0.50	0.19	0.13	0.73	0		0.0	0.0			0.10	0.20	Butanol+1NHNO_3 cont. 1% Antipyrine	P5
9.	0.10	0.24	0.18	0.08	0.18	0.77	0.65		0.43	0.42			0.15	0.63	Doxane, 100 ml; antipyrine, 1g; HNO_3, 1ml; Water, 2.5 ml.	P5
10.	0.73	0.65	0.17	0.1	0.29	0.16	0.16		0.09	0.84			0.18	0.34	Butanol, 50%; HAC, 10%; acetoacetic ester, 5%; Water, 35%	P6
11.	0.56	0.47	0.50	0.02	1.0	0.97	0.85	0.95	0.08T	1.0			0.16	0.94	Ethanol+10% 5NHCl[b]	L10
12.	0.35	0.28	0.66	0.06	0.84	0.88	0.77	1.0	0.05	1.0			0.03	0.84	Isopropanol+10% 5NHCl[b]	L10
13.	0.12	0.10	0.70	0.0	0.60	0.95	0.8T			1.05			0.0T	0.65	Butanol+1NHCl[b]	L10
14.	0.18	0.11	0.58	0	0.67	0.76	0.76T			0.84			0.17	0.63	Butanol+2NHCl[b]	D5
15.	0.42	0.31	0.83	0	0.97	1.0	0.99			1.0			0.39	0.76	Butanol+4NHCl[b]	D5
16.	0.72	0.52	0.94	0	0.99	0.98	0.95			0.99			0.55	0.79	Butanol+6NHCl[b]	D5
17.	0.98	0.58	0.92	0	0.97	0.89	0.83			0.97			0.52	0.68	Butanol+8NHCl[b]	D5
18.	0.98	0.58	0.84	0	0.90	0.83	0.77			0.90			0.45	0.58	Butanol+10NHCl[b]	D5
19.	0.97	0.57	0.78	0	0.81	0.78	0.73			0.83			0.40	0.50	Butanol+12NHCl[b]	D5
20.	0.02	0.02	0.41	0.0	0.23	0.52				0.55			0.0	0.22	Amylalcohol+2NHCl	L10
21.	0.42	0.26	0.43	0.02	0.75	0.83	0.77	0.96		0.82		0.98	0.03	0.67	45% Ethanol, 45% Isopropanol 10% 5NHCl	W6
22.	0.11	0.12	0.44	0.02	0.73	0.81	0.76	0.89		0.85		0.94	0.03	0.65	45% Isopropanol, 45% Butanol 10% 5NHCl	W6
23.	0.02	0.03	0.41	0.01	0.22	0.42		0.61				0.75	0.0	0.30	50% Butanol, 50% Amylalcohol saturated with 1NHCl	W6
24.	0.39	0.37		0.18	0.37		0.01T			0.7T			0.11	0.67	Ethanol, 90%; 8NHNO_3, 10%	L13
25.	0.35	0.20	0.45	0.24	0.22				0.30	0.45	0.09		0.07	0.39	Isopropanol, 180; HNO_3, 20; Water, 10	L8
26.	0.06	0.05		0.13	0.07	T	0			0.58T			0.02	0.03T	Isopropanol, 90; 8NHNO_3, 10	L13
27.	0.18	0.17		0.23	0.19					T	0.16		0.15	0.27	Butanol sat. with 10% aqu. HNO_3	L11
28.	0.06	0.10	0.45	0.12	0.10	0.74							0.01	0.18	Butanol sat. with 1NHNO_3	E3
29.	0.15	0.15	0.48	0.19	0.15	0.84							0.15	0.25	Butanol sat. with 3NHNO_3	E3
30.	0.01	0.02		0.06	0.03					0.64T			0.02	0.17	Amylalcohol sat. with 20% aqu., HNO_3	L13
31.	0.82-0.91	0.41-0.51		0-0.49	0.76-0.89	0.79-0.97	0.83-0.97	0.88-0.97	0.71-0.92	0.12-0.86	T		0.01-0.15	0.31-0.54	Methy n-propylketone 95 10NHCl5	C5
32.	0.89-0.98	0.65-0.76		0.26-0.57	0.82-0.93	0.86-0.99	0.91-0.98	0.84-0.93	0.84-0.91		0-0.19	0-0.19	0.12-0.23	0.41-0.60	Methyl n-propylketone 85 10NHCl 15	C5
33.	0.83-0.95	0.48-0.66		0.33-0.63	0.82-0.92	0.80-0.92	0.85-0.94	0.87-0.94	0.73-0.92	0.73-0.95	0-0.19		0.10-0.25	0.32-0.51	Methylisopropyl ketone 85 10NHCl 15	C5
34.	0.90-0.98	0.41-0.49	0.58-0.61	0.05-0.34	0.69-0.77	0.84-0.89	0.82-0.87	0.90-0.95	0.58-0.75	0.63-0.76	0-0.17	0-0.16	0.11-0.20	0.30-0.36	Methyl isobutyl ketone 85 10NHCl 15	C5

35.	0.11	0.10	0.54	0.0	0.80	0.83	0.90	0.67		1.00		0.93	0.40	0.80	Butanol, 100 ml; HBr, 10 ml; Water, 90 ml (Two Phases)	K10
36.	1.00	1.00	1.00	0.1-0.86T	1.00	1.00	1.00	1.00		1.00		1.00	0.60	0.92	Butanol fraction of #35+HBr, 20 ml	K10
37.	1.00	1.00		0.55-1.0T	1.00	1.00	1.00	1.00		1.00		1.00	0.65	0.78	Butanol fraction of #35+HBr. 60 ml	K10
38.	0.01	0.03	0.30	0-0.68	0.0	0.28	0.26	0.24		0.05	0.56T		0.0	0.02	Phenol shaken with 2$\underline{N}$HCl	L12
39.	0	0.68	0.68	0.90	0.76	0	0						0.10	0.0	S-Collidine shaken with water'	P6
40.	0	0.76	0.65	0.78	0.76	0	0.38		0	0			0	0	S-Collidine shaken with 0.4$\underline{N}$HNO$_3$	E3
41.				0.1						0.25			0.03		Butanol sat. with 1$\underline{N}$HNO$_3$ cont. 0.5% benzoylacetone	P5
42.				0.24					0.30		0.42		0.07		Isopropanol cont. 5% water and 10% HNO$_3$	L8
43.	0.76	0.46		0	0.63			1.0	0.96	0.80	0.11	0	0.48	0.93	Acetone, 95; 6$\underline{N}$HCl, 5[c]	W7
44.	0.70	0.60		0.40				1.0			0.26	0	0.16	0.93	Acetone, 95; 0.5$\underline{N}$HCl, 5[c]	W7
45.	0	0		0.44	0.76			1.0	0.80	0.82	0.26	0.26	0	0.98	Acetone, 90; 5% aqu. Tartaric acid, 10[c]	W7
46.	0	0		0.45	0.68			1.0	0.83	0.83	0.08	0.45	0.35	0.96	Acetone, 90; 5% Na_2HPO_4, 10[c]	W7
47.	0	0		0	1.0			1.0			0	0	0	1.0	Acetone, 80; Methylacetate, 20[c]	W7
48.	0	0		0.37	0.45			1.0	0.13	0.13	0	0	0	0.98	Acetone, 95; 10% aqu. Antipyrine, 5[c]	W7
49.	0	0		0	0.46			1.0	0.77	0.77	0	0	0.23	0.92	Acetone, 95; 5% aqu. thio acetamide, 5[c]	W7
50.	0	0		0.23	0.33			1.0	0.74	0.74	0	0	0	0.91	Acetone, 95; gl. HAC, 5[c]	W7
51.	0.85	0.97		0.96	0.75			0.71	1.0	1.0	0.71	0.71	0.81	0.91	5% aqu. Tartaric acid[c]	W7
52.								0	0.3	0.3	0.4	0.4	0.7	0	Water sat. with Aniline[c]	W7
53.	0.95	0.22	0.42	0.10	0.05	0.58	0.0		0.24	0.31			0.03	0.02	Butanol, 50 ml; 0.1$\underline{N}$HNO$_3$, 50 ml Benzoylacetone, 0.5g	E4
54.	0.0	0.78	0.64	0.79	0.78	0.0	0.38		0.0	0.0			0.0	0.0	Collidine, 50; 0.4$\underline{N}$HNO$_3$, 50	E4
55.	0.10	0.24	0.18	0.08	0.18	0.78	0.0		0.43	0.40			0.15	0.62	Dioxan, 100 ml; HNO$_3$1ml; Phenazone, 1g; water, 2.5 ml	E4
56.				0.25					0.0	0.81			0.50		t-Butanol, 40; Acetone, 40; water, 12; HNO$_3$, 8[a]	S14
57.		0.40			0.32					0.90			0.15	0.76	t-Butanol, 40; Acetone, 40; water, 11; 6$\underline{N}$HNO$_3$, 4.5; Acetylacetone, 4.5[a]	S14
58.	0.58-0.70			0.27-0.36	0.55-0.66					0.87-0.95	0.17-0.25		0.31-0.41	0.65-0.78	Ethylether, 50; Methanol, 30; water, 20; HNO$_3$, 2	P1
59.	0.49-0.59	0.44-0.53											0.18-0.29	0.66-0.75	Ethylether, 50; Methanol, 30; water, 22; HNO$_3$, 4	P1
60.	0.07	0.15	T	0.03	0.95	0.77				1.25	0.02	1.18	0.41	0.95	Butanol sat. with 10% HBr	L11
61.		0.44		0.36	0.39				0.69	0.69			0.24	0.51	Isopropanol, 80; gl. HAC, 10; water, 10[a]	B6
62.													(RaD 0.15 (RaE 0.5		Butanol sat. with 1$\underline{N}$HCl[a]	C6
63.													(RaD 0.27 (RaE 0.62		Butanol, 50; Propanol, 50; shaken with 7$\underline{M}$ LiNO$_3$, 2$\underline{M}$HNO$_3$[e]	L14
64.		0.85-1.0			0.85-1.0				0.85-1.0				0.0	0.0	4$\underline{N}$NH$_4$OH	I6
65.													0.0	0.88	0.4$\underline{N}$H$_2$SO$_4$	I6

[a] Circular paper used.

[b] Each solvent including the one-phase mixtures was prepared by shaking 100 ml of Butanol with 100 ml of the HCl solution.

[c] Vapor supersaturated with solvent.

[d] Other R_f values measured; Ni, 0.08; Po, 0.8.

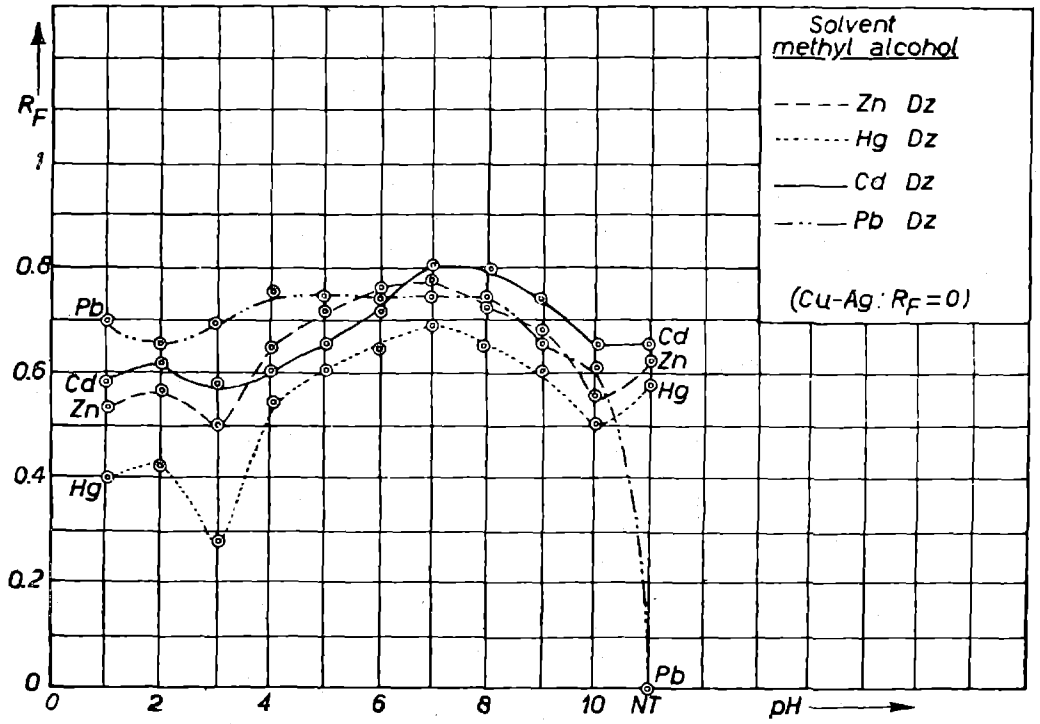
[e] Other elements separated on same chromatogram: Te, 0.47; Se, 0.72; Po, 0.97.

separated quickly and cleanly on a circular disc of filter paper that had been impregnated with an acetone solution of dithizone and dried in air (N5). The solvent used was 0.1 N nitric acid and acetone in 10:1 ratio with concentric rings of Hg, Cu, Bi, Cd and Pb appearing after the separation. It is notable that in this case the lead fraction moved with the solvent front ahead of the other elements. These data are not included in Table XX due to nonavailability of the R_f values for the various fractions.

A more detailed study of the use of dithizone in paper chromatography has been made by Venturello and Ghe (V4). In this work the papers were impregnated with buffer solutions of varying pH, the elements were put on the paper as dithizonates by evaporation from a dilute dithizonate solution and various alcohols were tried as solvents. Figure 38 shows the result with methanol solvent. Again at low pH values the lead moves ahead of the other elements but in the absence of buffer (point marked NT) the lead remained at the origin. This behavior suggests some very useful separations.

Paper chromatography has been used by a number of workers for separation of RaD(Pb^{210}), RaE(Bi^{210}) and RaF(Po^{210}) mixtures. Levi and Danon (L14) used a butanol-propanol mixture which had been shaken with a nitric acid, lithium nitrate solution (item 63, Table XX). Using Whatman No. 1 paper they obtained separation in 18 hours at room temperature. No difference in R_f values were obtained with or without weighable quantities of lead and bismuth carriers.

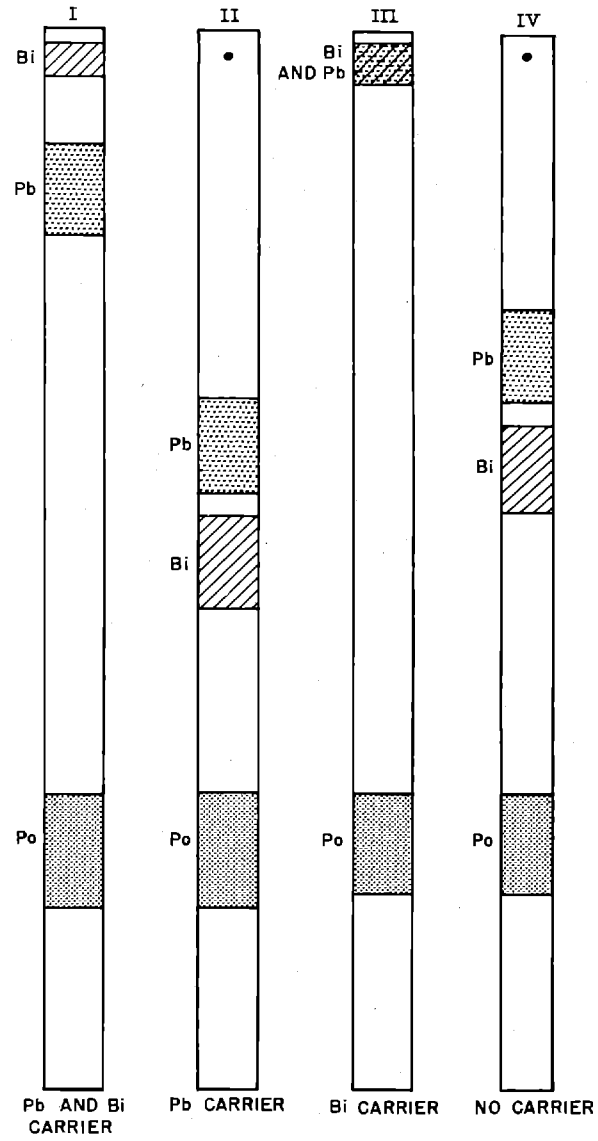
Frierson and Jones investigated the use of two solvent systems for RaD, E, F, separations. The first solvent mixture used was made up of 50 parts butanol, 15 parts pyridine, 5 parts hydrochloric acid, 10 parts acetic acid and 10 parts water. The second was 60 parts butanol, 12 parts hydrochloric acid and 1 part concentrated sulfuric acid. In both cases the presence of



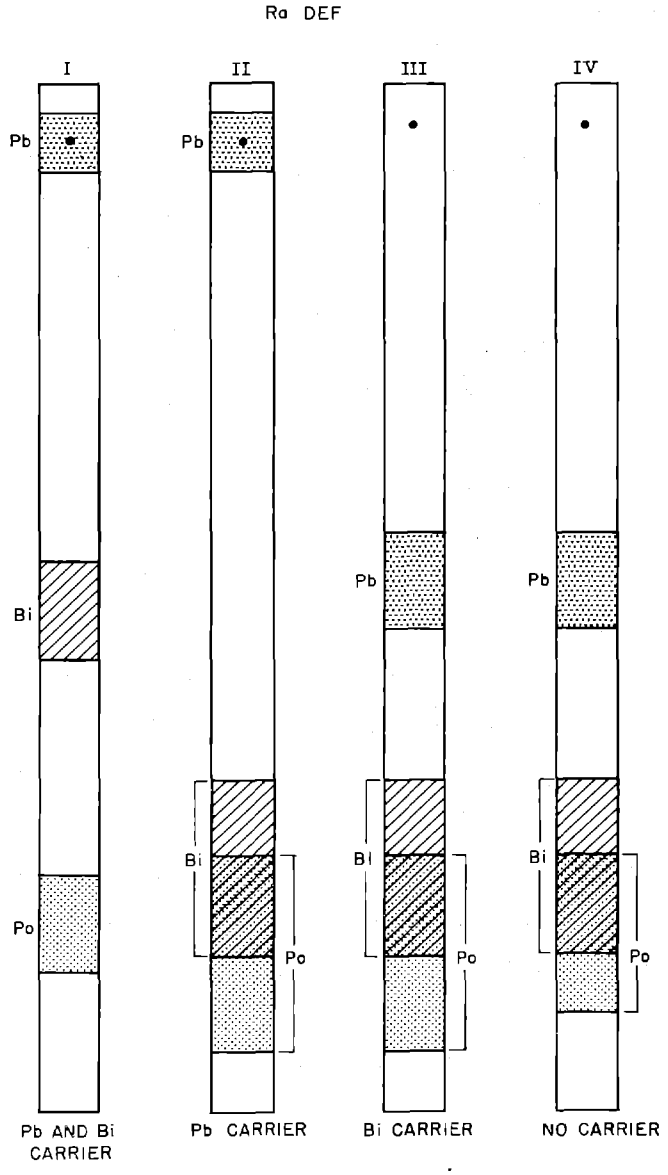
38. R_f values for chromatographic separations of a number of elements on filter paper as a function of pH for methyl alcohol solvent. From G. Venterello and A. M. Ghe, Anal. Chim. Acta 10, 335 (1954).

weighable amounts of lead or bismuth carrier influenced the separations obtained. The chromalograms for both sets of solvents are shown schematically in Figures 39 and 40.

Perhaps the most attractive feature of filter paper chromatography is the ability to make fast, quantitative separations of simple or complex mixtures. The use of circular paper with central solvent feed increases separation speed due to the two-dimensional flow of the solvent. In addition the solvent flow rate can be adjusted over moderate limits by charging the width and length of the tab or wick which delivers the solvent to the center of the paper (L15). By using circular paper Martin (M15) has separated lead from copper, arsenic, silver, cadmium, antimony, mercury and bismuth in



39. Representative chromatograms showing separation of RaD (Pb^{210}), RaE (Bi^{210}) and RaF (Po^{210}) and the influence of added carrier for butanol-pyridine-acetic acid solvent. From W. J. Frierson and J. W. Jones, Anal. Chem. 23, 1447 (1951).



40. Representative chromatograms showing RaD (Pb^{210}), RaE (Bi^{210}) and RaF (Po^{210}) separations and the influence of added carrier for butanol-hydrochloric acid-sulfuric acid solvent. From W. J. Frierson and J. W. Jones, Anal. Chem. 23, 1447 (1951).

90 minutes using a butanol-thiocyanic acid solvent on Whatman No. 41 paper (item 1 of Table XX). The solvent flow rate can be increased with attendent decrease in separation time by rotating the circular chromatogram during development at speeds up to 1800 rpm (I7).

The use of a solvent of high wetting power can also speed separations. By ascending capillary flow of methanol 5 volume per cent hydrochloric acid on 1.5 cm x 9 cm Whatman paper strips, lead has been separated from soil samples in 30 minutes (H13). The lead remained near the origin and was separated from bismuth, copper, cadmium, mercury, iron, aluminum, magnesium, zinc, cobalt, nickel, and tin which moved up the paper in a mixed band.

Warren and Fink (W7) have combined solvents of high wetting power, a thick absorbent paper having high wettability and supersaturation of the chamber with solvent vapor to achieve quantitative separation of microgram quantities of complex mixtures in 2-15 minutes. The solvents used were acetone containing varying amounts of complexing agents and are indicated in items 43 to 52 of Table XX. The paper used was 0.1 in thick Eaton-Dikeman Grade-301 which had been purified by downward percolation with nitric and acetic acid (see section B). Solvent vapors were introduced continuously during the development by passing air through a flask of the boiling solvent and into the chamber. It was found that the solvent moved about 20 cm in 15 minutes by ascending capillary flow and that for elements whose R_f values were separated by about 0.5 units or more, adequate separation could be attained in two minutes (W7).

E. Related or extended separation methods.

In some cases useful separations can be obtained by using more than one solvent in succession. The flow of the second solvent can be either parallel, antiparallel or normal

to the flow of the first. Pollard, McOmie and Elbeith (P5) have described a number of separations of this type. The workers recommend washing the paper with carbon tetrachloride and drying it between solvents (P5). A separation of mercury, lead, copper, bismuth and cadmium based on this principle and using inorganic solvents has been described by Imai (I6). The first solvent was 4 N ammonium hydroxide. The copper, mercury and cadmium moved along the paper (R_f values 0.85-1) and were separated from lead and bismuth which remained at the origin. The copper, mercury and cadmium were separated by developing with a mixture of 0.3 N potassium iodide and 0.5 N potassium carbonate normal to the direction of the first solvent. Lead and bismuth were separated by using 0.4 N sulfuric acid. Lead remained at the origin, bismuth moved close to the solvent front (I6).

A related technique in which a verticle paper strip is intercepted at intervals by horizontal strips normal to the main strip has been proposed by Tewari (T5). A single solvent is used and separations of lead from mercury, silver, copper and bismuth are described (T5).

In the presence of macroquantities of impurities it is sometimes desirable to use a column packed with a slurry of filter pulp instead of a regular paper. The order and relative positions of the various fractions for a given solvent can be estimated from the R_f tabulation. Microgram quantities of RaD(Pb^{210}) and RaE(Bi^{210}) and macroquantities of mercury and gold have been separated by this technique (F11). The mixture was loaded on a 40 cm x 17 mm diameter column of Whatman No. 1 ashless cellulose powder in a 3 N hydrochloric acid. The gold, mercury and polonium (RaF) came off first and quantitatively. About two column volumes later the carrier-free bismuth-210 (RaE) came off and finally, one or two column volumes later carrier-free lead-210 (RaD) was eluted. The entire procedure required about 90 minutes.

Migration of ions under the influence of an applied field on filter paper wet with various electrolytes has been studied by Majumdar and co-workers (M16)(M17). Using simple equipment and an applied bias of 150 volts for 5 hours some of the species have been observed to separate by more than 12 cm. Although a number of lead separations have been demonstrated (M16) this technique does not appear to offer significant advantage in speed or convenience over standard chromatographic procedures.

10. Electroanalytical separations.

Selective electrodeposition was used very early for separation of "radiolead" from radium or thorium samples. The early applications are reviewed in the book by Rutherford, Chadwick and Ellis (R5). More recent techniques and applications are covered by Lingane (L4).

Controlled Potential Analysis with Platinum Electrodes

Differences in the reduction potentials for copper, bismuth, lead and cadmium with a dropping mercury electrode has been seen in Figure 12. Similar differences exist if a platinum electrode is used providing a suitable depolarizing agent is employed to prevent excess polarization at the anode. Hydrazine hydrochloride or hydroxylamine hydrochloride are the usual depolarizers (L4).

Erbacher and Phillip have used 7% nitric acid solution for controlled potential separation of RaD(Pb^{210}) from old radium solutions containing large amounts of inactive impurities (E5).

It has subsequently been found desirable to control the pH of the solution and to introduce tartarate ion to prevent radiocolloidal formation of easily hydrolyzed species (such as Sn and Bi) (L4). Conditions for successive, quantitative separation of copper, bismuth, lead and tin by controlled potential deposition onto a platinum cathode has been deter-

mined by Lingane and Jones (L16). The separation was carried out from a 0.25 M tartarate solution to which 1 gram of hydrazine hydrochloride had been added per 100 ml. of solution. The solution pH was adjusted to 5.8-6.0 and copper was deposited at -0.30 volts vs. a standard calomel electrode (S.C.E.), bismuth was deposited at -0.40 volts and lead at -0.60 volts. The solution was acidified to pH 2 or less and tin was deposited at -0.60 to 0.65 volts. The cathode was removed while rinsing with distilled water after each deposition was complete (indicated by reduction of current to a constant minimum value) and a clean electrode introduced. The separation takes about four hours for up to 100 mg amounts of each metal (L16). Moderate amounts of nitrate or sulfate were not found to be objectionable.

Alfonsi indicates that it is advantageous to add succinic acid (making the solution 0.1 M) to the solution in separation of copper, lead, antimony and tin (A1), and to begin the lead deposition at -0.60V vs S.C.E. increasing to -0.65V at the end of the lead deposition. He has used this method to separate lead from tin from lead-tin solders (A3). Under similar conditions (0.1 M succinic acid, 0.1 M KCl, 0.06 M hydrazine and 0.3 M tartaric acid, pH 5.9). Ishibashi, Fujinaga and Kusaka have studied the completeness of the separations and the recovery yield for lead and bismuth by using ThB(Pb^{212}) tracer (I8). They find the mutual separations to be good for up to 50-100 mg of each of copper, bismuth and lead although a small amount of lead remained in the solution.

An attempt to make the separation even more selective for bismuth and lead by addition of ethylenediaminetetraacetic acid (EDTA) to the solution has been reported (H14). In this method, the bismuth was deposited on the cathode from a pH 3.5-5.5 dilute nitrate solution to which a slight excess of EDTA had been added at about 60°C with a voltage of 1.2 volts.

After adjustment of the pH to 6-7 the lead was deposited at 40° and a voltage of 2.5-4 volts (H14).

In attempting to separate carrier-free ThB(Pb^{212}) and ThC(Bi^{212}) from old thorium samples Harrison, Lindsey and Phillips found that in order to maintain the correct cathode potential, lead and bismuth carrier had to be added to the solution (H15). The amount of inert material required was not great, however, and as low as 10^{-15} grams could be plated onto the cathode successfully. Rogers has also investigated the separation of ultramicrogram quantities by controlled potential analysis and finds that the optimum deposition potential can change as much as 0.5 volts in going from macro "multilayer" deposits to fractional monolayer deposits (R6). It was also found that codeposition of macroquantities of other matieral could also alter the deposition behavior of trace constituents.

One of the attractive features of controlled potential separations is that the deposit can often be used directly for radioactivity measurements (R3). An example of tailoring the shape and size of the cathode to fit a given counting requirement is shown in Figure 41 which shows the plating cell and cathode configuration employed by Harrison, Lindsey and Phillips (H15). The disc shaped platinum cathode was pressed into a disc of heat-softened polyethylene to prevent the ThB(Pb^{212}) from depositing onto both sides.

Under suitable conditions, lead can be deposited onto the anode as PbO_2. This appears to be selective and has been used for lead purification (E5)(U1). The optimum condition for anodic deposition from nitric acid solution is 5-9% nitric acid with about 2.5 volts applied (U1). The PbO_2 can be easily removed from the platinum anode by addition of HNO_2 (E5) or dropwise addition of hydrogen peroxide to a nitric acid solution.

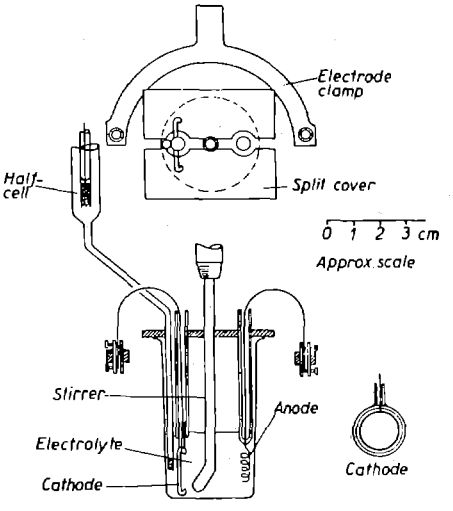


Figure 41

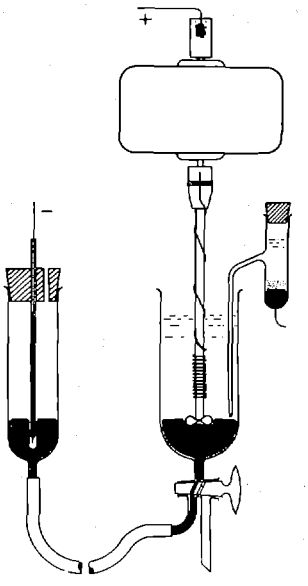
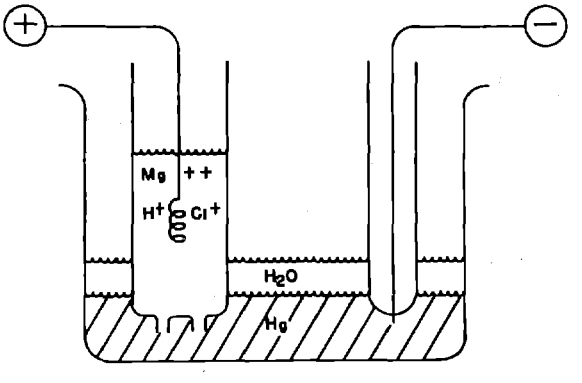


Figure 42

41. Plating cell and platinum disc cathode for controlled potential separations. From A. D. R. Harrison, A. J. Lindsey and R. Phillips, Anal. Chim. Acta 13, 459 (1955).

42. Electrolysis cell for controlled potential separations with a mercury cathode. From J. J. Lingane, "Electroanalytical Chemistry", Interscience Publishers Inc., New York, 1953.



43. Electrolysis cell for controlled potential electrodeposition into a mercury cathode and simultaneous removal of the electrodeposited material into aqueous solution. From M. Chemla and J. Pauly, Bull. Soc. Chim., France 20, 432 (1953).

Controlled Potential Analysis with a Mercury Electrode

The reversability and reproducability of mercury electrodes can be used to advantage for controlled potential separations. It has been found that the potential at which half the element is deposited agrees closely with the polarographic half-wave potential (I9)(L4). The polarographic trace shown in Figure 12 can therefore define the conditions for clean and quantitative separations of copper, bismuth, lead and cadmium from a 0.5 M tartarate solution. Such separations combined with polarographic determinations have been used by Lingane for separation of these four elements in a cell of the type shown in Figure 42 (L4). The anode used was a silver wire wrapped around the stirrer shaft.

A disadvantage of a mercury cathode is the necessity of removing the desired product from the mercury before radioactivity measurements can be performed. This, of course, is not a problem if an unwanted impurity is being removed as in the removal of macro amounts of copper shown in Figure 12. Lead can be removed from the mercury by shaking with a suitable oxidizing solution. Another technique which would seem to warrant further investigation is to use a cell which allows the desired activity to be removed from the mercury continuously during the deposition. Such a cell has been used for separation of carrier-free sodium-22 from magnesium solutions by Chema and Pauly and is shown in Figure 43 (C7).

Internal Electrodeposition

If a nickel foil or nickel powder is stirred in a dilute (0.5 M) solution of RaD(Pb^{210}), RaE(Bi^{210}) and RaF(Po^{210}) the bismuth and polonium will deposit on the nickel leaving the lead-210 in solution (R5). This has been used for separation of bismuth isotopes from lead cyclotron targets (M18). Gold, mercury, platinum, copper, silver, palladium and antimony also deposit.

If a silver foil is used polonium (RaF) deposits in high yield (R5). Thus RaD, E, F can be separated from each other by first stirring with a silver (to remove RaF) and then a nickel (to remove RaE) foil. The lead can be removed from the resultant solution by electrodeposition (B7).

The deposition of bismuth onto nickel has been used by Friedlander to achieve rapid separation of the 0.8 second half-life lead-207m isomer (F12). After adsorption of a cyclotron produced bismuth fraction (containing bismuth-207) onto nickel powder in a sintered glass funnel, the lead-207m daughter was separated rapidly and in high purity by flowing 0.5 N hydrochloric acid through the funnel directly to a scintillation detector.

Separation of bismuth and polonium from lead can also be achieved by immersing a hydrogen soaked platinum electrode in a 0.1 M hydrochloric acid solution of the tracer lead, bismuth and polonium (E6). Nitric acid, bromine or other substances which might poison the platinum electrode for adsorption of hydrogen must be absent. This has been used for separation of RaD from RaE and RaF (E6)(H5). This method does not introduce nickel or silver contamination into the RaD solution or in the RaE or RaF when these are dissolved from the electrode.

Thin ThB(Pb^{212}) Samples

Carrier-free deposits of ThB(Pb^{212}) can be conveniently prepared by collecting the ThB on a negatively charged platinum, aluminum or gold wire or foil suspended over a thorium deposit. The 52 second rare-gas member of the thorium decay chain Rn^{220} escapes from the thorium deposit and decays to shortlived Po^{216} which then decays to ThB(Pb^{212}) (see Figure 2). The charged recoil atom is collected on the electrode. The highest efficiency (20%) of collection of the thorium B was achieved by Morimoto and

Kahn (M23) with a potential of 1200 volts on the collecting plate. Variation of the spacing between the plate and the source between 0.5 and 1.5 inches produced no significant change in the amount of activity collected. Increasing the relative humidity from 30 per cent to 80 per cent at 25°C produced a seven-fold increase in collection efficiency for a solid thorium salt source (M23).

11. Volatilization separations.

Lead can be separated from rocks, minerals and meteorites by volatilization in a vacuum (M11)(I2). The lead is volatilized at 1300-1400°C from carbon crucibles and can be collected on a water cooled, quartz tube. Concentrated nitric acid dissolves the lead deposit.

12. Miscellaneous.

A. Carrier-Free lead.

Separation of carrier-free lead samples from inert or radioactive contaminants present in macro or tracer quantities can be accomplished by any of a number of the ways that have been outlined in the foregoing sections on techniques. Ion exchange (K8), solvent extraction (R7), and filter paper chromatography (F10)(F11) have all been used for separation of carrier-free radioisotopes. A precipitation separation of carrier-free lead from thallium oxide cyclotron targets has also been proposed (G6) (W8). In this procedure, the target material is dissolved in nitric acid, sulfurous acid is introduced to reduce the thallium to the univalent state, the lead is carried on a iron-III hydroxide precipitate by addition of iron carrier and ammonium hydroxide. After dissolution of the hydroxide in hydrochloric acid, iron was extracted into ethyl ether leaving the carrier-free lead in aqueous solution.

This discussion will be concerned with production of carrier-free lead radioisotopes, purity and purification of

reagents, and storage and handling of carrier-free lead solutions.

Sources of Carrier-Free Lead Radioisotopes

The most common supply of carrier-free lead radioisotopes has been natural radium or thorium samples. Due to the presence of appreciable amounts of stable lead in pitchblend which is the principle source of radium or in thorium ores it is necessary to obtain the carrier-free material from a sample which has previously been purified from lead. A convenient separation is that of diffusion of the noble gas member of the radium or thorium decay chain from the parent material and its subsequent decay to radioactive lead isotopes. Very early in the studies of radioactivity it was found that very high specific RaD(Pb^{210}) sources could be obtained by removing the "emenation" (Rn^{222}) (see Figure 1) from a radium solution into a closed glass flask, allowing it to decay, and dissolving the RaD(Pb^{210}) from the walls of the collecting flask (S18). The practice for many years of concentrating "emenation" into tubes or vials for medical use led to a rich source of RaD from "spent emenation tubes" (B7). The diffusion of Rn^{220} from thorium samples (apparently most efficient from thorium hydroxide precipitates) can also be used to provide a source of tracer-free ThB(Pb^{212}). Due to the shorter half-life of Rn^{220} (52 seconds) than its analog in the radium chain it is convenient to collect the ThB directly on a negatively charged wire or plate suspended above the thorium sample (H5).

The presence of radioactive decay products in lead sources or tracers obtained from natural sources is undesirable for some applications. A number of lead isotopes can be produced in carrier-free form and in high yield by helium-ion bombardment of mercury or by proton or deuteron bombardment of thallium targets. The isotopes prepared in this way and the relevant reactions are indicated in Table I.

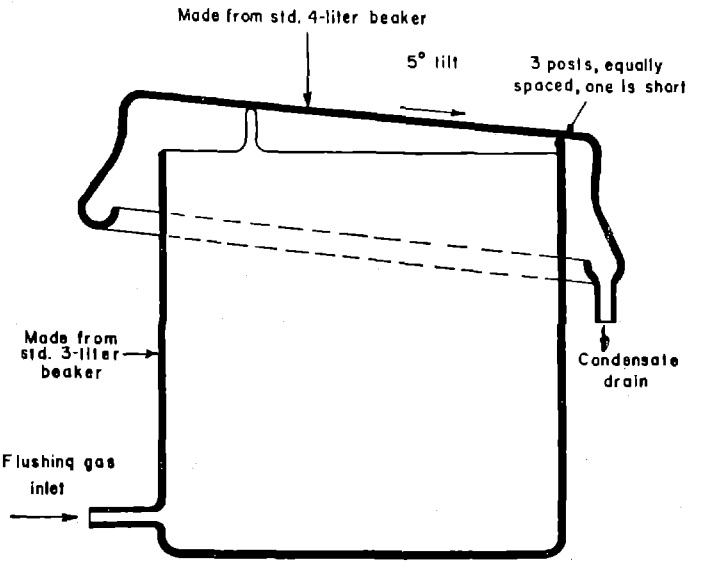
Perhaps the most useful cyclotron produced lead isotope for tracer use in terms of half-life and decay characteristics is 52 hour, lead-203. This isotope has been prepared by deuteron irradiation of thallium-oxide powder by Garrison and Hamilton (G6) who report the thick target yield of 1.5 microcuries per microampere hour of irradiation (for short, 10 hour or less, irradiations) when 19 Mev deuterons are used. The isotopic ratio of lead-203 to other lead isotopes produced is 3.4:1. Stable lead-204, produced by a (d,n) reaction is the principle other contaminant. The availability of high current proton accelerators (G8) make the $Tl^{203}(p,n)Pb^{203}$ reaction an attractive tool for production of high activity carrier-free sources of lead-203.

Reagent Purity and Purification

Depending on the degree of purity required, the procedures necessary to exclude extraneous lead carrier can be extremely involved or rather simple. The methods devised to obtain extremely high purity samples will be reviewed. For most (but not all) radiochemical applications of even so-called "carrier-free" samples such precautions are unnecessary. Consequently, the purity obtainable by less refined techniques will be indicated where such information is available.

It should be noted from the outset that one of the most serious and bothersome sources of lead contamination is from volatile lead substances present in the air and in airborne, lead-bearing, particulate matter. This airborne lead is due in large part to the widespread use of lead in motor fuels. It is therefore necessary that all equipment and glassware be cleansed thoroughly with specially purified acids and/or water before use. Also, prolonged exposure of the sample to the air should be avoided if very high purity is required. It is especially important that long evaporations and digestions be avoided (T6). For preparation of carrier-free lead samples for mass-spectrographic

analysis, Chow and McKinney (C8) found the following control measures necessary: lead-laden dusts and aerosole were removed from the laboratory air by electrostatic precipitation and filtration; laboratory floors were flushed with water twice weekly and gelatin step pads were placed at laboratory entrances; glassware and solutions were covered with "parafilm"; and solutions being heated and evaporated were contained in borosilicate glass or teflon containers (C8). The borosilicate glass evaporator tank and cover used by Chow and McKinney is shown in Figure 44. A similar evaporation chamber has been used by Thier (T6).



44. Borosilicate glass evaporator tank and cover. From T. J. Chow and C. R. McKinney, Anal. Chem. 30, 1499 (1958).

The results of experiments conducted to determine the magnitude of lead contamination from the air are shown in Table XXI. In these experiments, 500 ml of 6 N hydrochloric acid was taken to dryness in the various environments in the time period listed in the table. The evaporations performed in the ordinary-air laboratory were in a Transite hood recently coated with Tygon paint (C8).

Table XXII

Lead contamination from air.

Beaker	Condition	Laboratory	Time Days	Amount of Lead, γ
Teflon	open	ordinary air	8	4.07 2.32
	nitrogen-flushed container	ordinary air	8	1.13
	open	pure air	8	0.44
	nitrogen-flushed container	pure air	8	0.18 0.13
		pure air	1	0.02
Borosilicate glass	nitrogen-flushed container	pure air	1	0.03

From ref. C8.

Soft-glass often used for storage of mineral acids or prepared reagents and solutions is a common source of lead contamination. Borosilicate glass has also been found to yield traces of lead (S5). The use of silica (S5), teflon (C8) or platinum (T6) ware for heating and manipulating solutions reduces lead contamination from borosilicate glass. On the other hand, Chow and McKinney found that use of borosilicate glassware introduced no more than 0.1 γ of lead per analysis and use of borosilicate-glass is considered satisfactory for all operations and reagent storage and purification in determination of lead in foodstuff (L7) and biological samples (A1). Polyethylene bottles have been found useful for storage of reagents and solutions (T6).

Regular laboratory distilled water often contains lead in concentrations up to 0.1 parts per million. Passage of the distilled water through ion exchange resin is effective in removing lead contamination. One passage through a bed of amberlite IR-100 cation exchange resin has been found to reduce the

lead content of laboratory distilled water with an initial lead concentration of 0.055 parts per million to a concentration of less than 0.0015 parts per million (S5). After five passes through the resin the concentration was measured at 0.0010 parts per million. Thiers (T6) has found that Boston tap water passed through a 1.5 meter column of mixed IR-120 and IRA-410 resins (Rohm and Haas Co.) showed only 0.02 parts per billion lead contamination. For many purposes redistillation from a borosilicate glass still is adequate (A1) this can yield water of 0.0025 ppm lead content from initially 0.055 ppm water. Use of a fused silica distillation apparatus can give water containing less than 0.1 ppb lead contamination (M19). Some of the procedures used to remove lead contamination from common reagents are outlined below:

Hydrochloric Acid

Reagent grade hydrochloric acid contains up to 0.03 ppm of lead (S5). Solution of anhydrous hydrogen chloride gas in purified water is the usual method of obtaining the pure acid (C8). Scrubbing the gas twice in a bubble tower with triply distilled water before dissolution reduces the lead concentration to 0.06 ppb (T6). Very pure hydrochloric acid can also be obtained by isothermal distillation, e.g., by placing a dish of concentrated hydrochloric acid and a dish of pure water (in platinum, silica, or polyethylene) side by side in an empty desiccator and allowing to stand for a day or so (S5).

Nitric Acid

Up to 0.01-0.03 ppm of lead is commonly encountered in reagent grade concentrated acid (S5). Redistillation of the azeotrope (65% HNO_3-H_2O) is generally used for purification. Redistillation in a borosilicate-glass still gives adequate purification for many purposes (A1). If an extremely pure produce is required (< 1 ppb) the use of a fused silica condensor has been proposed (M11) but significant quantities of lead (at this level

of purity) has still been found to result (T6). Thus nitric acid is one of the hardest purification problems.

Hydrofluoric Acid

Strontium fluoride precipitates will carry lead fluoride with high efficiency and can be used to purify hydrofluoric acid solutions. The lead content can be reduced from 2 ppm of lead (not uncommon for reagent grade HF) to less than 0.002 ppm of lead by addition of 10 ml. of strontium chloride per kilogram of hydrofluoric acid and filtration of the supernatent solution.

Other Acids

Sulfuric, sulfurous, perchloric, hydrobromic and acetic acids can be purified from lead by distillation in a borosilicate glass or silica distillation apparatus, giving purity in the parts per million or parts per billion range respectively (T8).

Ammonium Hydroxide

Solution of anhydrous ammonia gas in pure water gives a high purity product (T6). Very pure ammonium hydroxide solutions can be made by isothermal distillation as noted above for hydrochloric acid. Ammonium hydroxide is best kept in polyethylene or ceresin-lined bottles (S5).

Soluble Salts

Soluble salts may be purified by recrystallization in many cases or if the salt is soluble in weakly basic solution by extraction of lead contamination into dithizone dissolved in carbon tetrachloride or in chloroform.

Organic Reagents

In general, organic reagents as obtained in reagent grade quality are much freer of lead contamination than inorganic

reagents. Distillation or recrystallization will usually yield a very pure product. Purification of dithizone has been outlined in section IV-6-B.

Storage of Reagents and Solutions

Interference with carrier-free lead determinations can arise during storage of reagents or of tracer lead solutions by (1) contamination of lead from the container, (2) loss by adsorption of tracer lead on the container or (3) contamination by desorption of previously adsorbed ions.

Contamination of standard pH 2 nitric acid solution stored in soft glass (Kimble), borosilicate glass (Pyrex, 774) and polethylene (Plax) containers for twelve months has been investigated by Thiers (T6). The results of this study are shown in Table XXII. The polyethylene container was found to be the only one of the three that did not introduce lead (as well as other) contamination. Preiss and Fink have noted that up to 0.1 mg of solids can be removed per 100 cm^2 of Pyrex glass in a 72-hour exposure to 15% hydrochloric acid (P7). Similar results have been obtained for storate of 0.1 N sodium hydroxide solution (T6).

Loss of tracers from solution by adsorption on the container can occur from acidic as well as basic solutions and is a function of the type of container used. Using a number of elements which are not picked up from glass containers in storage, Thier found loss of nickel, manganese, molybdenum, vanadium, gold, platinum, ruthenium, and titanium when stored in 6% mineral acids in glass (soft glass or borosilicate glass) for 75 days (T6). A smaller number showed losses when stored in fused quartz and none showed losses when stored in polyethylene. In storage of radioactive tracers, loss of the tracer on the walls and contamination of the solution with inert material can occur simultaneously. Polyethylene containers are recommended for storage of reagents and solutions where possible.

Table XXII
Contamination of acid solutions by container materials during 12 months' storage.

Contaminating Elements From		
Pyrex (774)	Soft Glass (Kimble)	Polyethylene (Plax)
Al, B, Ca, Fe, Pb, Li, Mg, Mn, Na, Si, Sr	Al, B, Ca, Pb, Li, Mg, Na, Si, Sr	none

From ref. T6.

It is important when working with ultra-micro amounts of material, never to use glassware or containers which have been used for macro amounts of material especially of the same element. Even involved cleaning procedures have been found to leave prohibitive amounts of material on the container.

B. Gaseous lead samples.

It is sometimes desirable to prepare gaseous compounds of lead for mass spectrographic analysis or for measurement of decay characteristics. In particular the study of long lived (5×10^7 yr) lead-205 which decays by electron capture unaccompanied by gamma ray emission or of other electron-capture isotopes is facilitated by the use of a gaseous source which can be introduced directly into the counting chamber for increased detection efficiency.

Convenient methods for preparation of volatile tetramethyl lead have been developed. Most workers have used the reaction of lead-dihalide with the grignard reagent. The equation for this reaction is:

$$4\ CH_3MgX + 2\ PbX_2 \longrightarrow (CH_3)_4Pb + Pb + 4\ MgX_2$$

Lead tetramethyl results in fifty per cent yield. After separation of lead from mineral samples, Bate, Miller and Kulp (B8) then treat the dichloride with excess methyl grignard reagent to accomplish the conversion. The excess grignard reagent is then

hydrolyzed and tetramethyl lead is separated from the aqueous solution into ethyl ether. Separation from the ether is accomplished by fractional distillation (B8).

A superior method, in terms of yield, for preparation of tetramethyl lead utilizes reaction of lead dihalide with methyl lithium reagent and methyl iodide (G7). The general equation for this reaction is:

$$3CH_3Li + CH_3I + PbX_2 \longrightarrow (CH_3)_4Pb + 2\ LiX + LiI$$

V. Dissolution of lead samples.

Lead metal is easily dissolved in nitric acid. Lead dioxide which is occasionally used for cyclotron targets or is sometimes produced during separations by anodic oxidation can be dissolved in nitric acid by dropwise addition of hydrogen peroxide.

Lead can be recovered from mineral samples by sodium peroxide fusion (R3)(R8) followed by dissolution of the melt in nitric acid. For many rock and soil samples, leaching with hot dilute (L:3) nitric acid (H13) or with hot concentrated sulfuric acid followed by nitric acid (P2) or with a sulfuric acid-hydrofluoric acid mixture (I2) has been found to be adequate. Use of sulfuric acid should be avoided in samples containing large amounts of calcium. The use of hydrochloric acid to dissolve or leach mineral samples frequently gives incomplete lead recovery due to the presence of lead minerals (pyrite, chalcopyrite, barite, etc.) which are insoluble in hydrochloric acid (S19). Quantitative lead recoveries of lead from rocks, minerals, stone meteorites and iron meteorites by volatilization at 1300°-1400°C in a carbon crucible in a vacuum has been reported (I2)(M11). The lead in micro or macro quantities can be collected on a cooled quartz tube (M11).

Methods for recovery of lead from biological samples have been frequently described and much discussed in the litera-

ture. Teapot wars have been waged between dry-oxidationists and wet-oxidationists, between properchloric acid users and antiperchloric acid users. According to Gorsuch (G4), of 250 investigations reported in the literature, 51 per cent used wet digestion with the remaining 49 per cent using ashing procedures. Critical reviews appear to convince few except the reviewer of the efficacy of a "preferred" method. There are apparently a number of techniques which can be used for quantitative recovery of traces of lead from biological or other organic samples. These will be briefly reviewed, the advantages and disadvantages of each will be pointed out when known. The most comprehensive review of the subject is the recent paper by Gorsuch (G4).

Direct oxidation by nitric and perchloric acids have been used by many workers. Such methods have been shown to give quantitative lead recovery from a wide variety of samples (G4). The use of perchloric acid is considered unsafe by some (M20). This worker has found nitric and perchloric effective for recovery of lead from cellulose but less easily handled if the sample contains much animal fat. A scheme for controlling the oxidation by perchloric acid by controlling the temperature has been proposed by Smith (S20). By refluxing the vapors, the concentration of perchloric acid can be kept constant and increased in small, carefully controlled stages. The boiling point of the solution is used to indicate the perchloric acid concentration at each stage of the process (S20). An advantage of wet digestions generally and nitric and perchloric acid digestions in particular is their convenience and speed (5 to 30 minutes) as well as the complete lead recovery obtained. A possible disadvantage is the large quantities of nitric acid sometimes required with attendant contamination by lead in the acid.

Sulfuric acid digestion either alone or in conjunction with nitric acid has been used to dissolve organic materials without

the danger which sometimes accompanies the use of perchloric acid. Such dissolution methods often lead to loss of lead. The mechanism of loss is principally coprecipitation of lead on insoluble residues as lead sulfate. The amount of loss is somewhat dependent on the amount of calcium present. Up to 70 per cent of the lead has been lost in dissolving dried milk samples in the presence of sulfuric acid (G4) and losses of up to 10 per cent were observed for samples having a comparatively low calcium content. In general the use of sulfuric acid should be avoided if quantitative lead recovery is sought.

An exception to the above reservation about the use of sulfuric acid appears to be in the method of Middleton and Stuckey (M21). In this method the oxidation is done principally by nitric acid with a small amount of sulfuric acid added to moderate the reactivity of the "char" and thereby prevent ignition. The oxidation is started with nitric acid as concentrated as can be tolerated without excess violence (50% is recommended) to which a small amount of sulfuric acid (~ 2 ml) has been added. This is evaporated until the nitric acid is removed and a black "char" remains. Fuming nitric acid is then added until the oxidation is complete. This method has been shown by radioactive tracer methods to give complete recovery of lead in samples containing low levels of calcium (G4)(M21) but should probably be avoided if large amounts of calcium are present. The main disadvantage of the use of nitric acid alone is the possibility of self-ignition of the blackened residue after evaporation of the initial nitric acid solution. This ignition, which leads to serious losses of lead and other volatile constituents, is often initiated by addition of fuming nitric acid to the "char". It is the experience of the author that addition of dilute nitric acid followed by small amounts of perchloric acid reduces the danger of self-ignition of the residue and introduces the perchloric acid at a stage in the process where the danger

of a violent reaction is substantially reduced.

Ashing procedures of many kinds have been described in the literature. These are frequently time consuming and can introduce considerable error by either lead loss or contamination. Some of the factors affecting lead recovery are:

1. Temperature of oxidation. Loss of lead, except in the presence of chloride, appears to be unimportant at temperatures below 450°C in the absence of sulfate ashing acids (L7)(G4)(A4)(P8) and below 550°C for sulfated samples (A4)(G4). Above 550°C the losses by retention on the crucible (at least with silica) as well as from volatilization increase sharply (G4).

2. The chemical and physical nature of the organic material can effect the behavior of lead. The presence of chloride either as ion or as organically bound chlorine can lead to serious losses of lead even at temperatures below 450°C. Addition of sulfuric acid reduces the loss in the presence of chloride ion but has little effect in the presence of covalently bound chlorine. This suggests that all dry oxidations should probably be avoided if chlorine is present or suspected in the sample.

3. The crucible material used or its history can influence the amount of lead tracer retained by the crucible after dissolution of the ash. Under rather extreme conditions (lead present as nitrate, heated to 630°C for 16 hours), Gorsuch (G4) found retention of up to 74 per cent on new silica crucibles, 24 per cent on used silica crucibles and 2 per cent on used platinum crucibles.

4. Ashing aids have been found to be unnecessary unless the ash content of the sample is low in which case addition of a few mg of magnesium nitrate or boric acid is beneficial (G4)(L7). The use of nitric acid gives a clean ash readily soluble in hydrochloric acid but if added when much carbon is present it can lead to much deflagration and loss of lead. The use of sulfuric acid tends to retard the oxidation of the organic

matter but lessens the chance of loss of lead by volatilization. In the latter case dissolution of the lead sulfate produced presents no problem unless large amounts of calcium are present.

5. Contamination of a carrier-free sample by airborne contamination during the long charring and ignition periods must be considered in some cases. Thiers (T6) has proposed the following method to avoid this difficulty: the sample is placed in a clean platinum container and placed under an evaporation cover and on a hot plate through which a current of filtered air or nitrogen gas is passed. A 250 watt infrared lamp placed above the glass cover is used to dry the sample slowly at first until the water has evaporated and the sample appears dry and brittle. The heat from the lamp is then augmented by heat from the hot plate under the apparatus until the sample assumes a charred appearance. The platinum dish is then placed in a silica-lined muffle furnace at 250°C or less. The temperature is increased slowly to 450°C and kept there until the sample is ashed completely.

Lead can be recovered from ashing residues by boiling in 6 N hydrochloric acid and filtering the supernatent liquid (T6) (P8)(L7). The use of sulfuric acid during the ashing does not appear to interfere with complete lead recovery by this method (A4)(G4).

VI. Counting techniques.

The lead isotopes most often used as tracers are lead-203, lead-209, lead-210 (RaD), and lead-212 (ThB). Counting techniques for these isotopes will be outlined but the same techniques can be adapted to other lead isotopes which may be encountered.

Lead-203, produced by the reaction of protons or deuterons on natural thallium or helium ions on mercury-201, is useful for carrier-free tracer studies. Counting of the 279 kev

gamma radiation in a scintillation detector is the most convenient detection method. The alternative is to count the X-rays and auger electrons resulting from the electron capture decay in a windowless proportional detector with the attendant difficulties imposed by absorption of the low energy radiations in the source material.

Lead-209, produced by neutron capture in lead-208 is a pure beta emitter with beta end point energy of 0.635 Mev. Measurement of the beta counting rate requires that corrections for self-scattering and self-absorption in the source be applied in order to get consistant results between duplicate samples of different weight (N6)(B9). In cases where absolute disintegration rates are required, counting in a 4-pi gas-flow proportional detector is recommended. A number of articles are available which describe the 4-pi beta counting technique (P9)(L17)(M24). The primary requirement is that the sample be as weightless as possible. A number of techniques for chemically separating carrier-free samples are described in sections IV and VII of this report.

Lead-210 (RaD) is difficult to measure directly because of the low energy of the beta particles (17 kev) and gamma radiation (47 kev, largely converted) accompanying its decay. Whenever possible it is desirable to measure the 1.15 Mev beta radiation of the daughter, bismuth-210 (RaE). The half-life of bismuth-210 is 5.0 days so it achieves effective equilibrium with the lead-210 in a one to two month period following the final lead-bismuth separation. Counts made before equilibrium is attained require that suitable corrections for daughter-growth be applied (F13). In some cases, it is convenient to count the 5.31 Mev alpha particles from the polonium-210 (RaF) granddaughter. This requires that the source be thin and because of the long half-life of polonium-210 (138 days), granddaughter-growth corrections (F13) are almost always required.

Lead-212 (ThB) can be counted directly by the 0.355 and 0.589 Mev beta particles or the 0.239 Mev gamma ray in its decay. The low energy of the beta particles and the high absorbing power of lead samples make reproducible or accurate counting, by using the beta particles alone, very difficult because of large and uncertain corrections due to absorption in the sample (N6)(B9). Scintillation counting of the 239 kev gamma radiation is preferred. Absolute counting rates can be conveniently obtained with high precision by use of 4-pi beta-gamma coincidence techniques (C9). For thin samples, detection of the 6.09 Mev alpha particles from the bismuth-212 (ThC) daughter or the 8.78 Mev alpha particles from the polonium-212 (ThC') granddaughter is especially attractive. Both the daughter and granddaughter activities reach equilibrium with the lead-212 within twelve hours after separation and the alpha particles can be detected with high precision and accuracy in a windowless or thin-window proportional counter. An attractive feature of the alpha particle detection is that background radiation due to natural beta emitters or cosmic radiation can be eliminated by setting the detector discriminator level to detect only the energetic alpha radiation.

For beta particle counting, lead samples are frequently weighed and mounted on filter paper or in counting planchets as lead chromate or lead sulfate. It is convenient when gamma radiation can be measured, to use a well-type scintillation detector. In this case the sample can be left in solution, perhaps even in the solution used for one of the sensitive colorimetric yielding methods outlined in section IV-6. Final separation of lead by controlled potential electrodeposition (or gaseous electrodeposition in the case of ThB) as outlined in section IV-10 can result in a stable, thin, uniform sample that can be counted directly (H15). If a chemical yield is required, this can be obtained either by weighing the counting plate before

and after the deposition or perhaps better, by a colorimetric method after the counting is completed.

VII. Collected radiochemical procedures.

A. Procedures for milking lead daughter activity from bismuth or polonium parents.

Procedure No. 1. Anion exchange separation of short-lived carrier-free lead isotopes from bismuth parents..... Stockendal, et.al.

Procedure No. 2. Precipitation separation of lead from bismuth parent activity.....Neumann.

Procedure No. 3. Separation of lead from polonium parent activity.....Karraker.

B. Separation of lead from natural sources, mostly carrier-free.

Procedure No. 4. Separation of RaD(Pb^{210}) from old radon ampules by dithizone extraction.....Boussieres and Ferradini.

Procedure No. 5. Electrolytic separation of ThB(Pb^{212}) from thorium nitrate.....Harrison, et.al.

Procedure No. 6. Rapid separation of carrier-free RaD(Pb^{210}) from Pt, Au, Po and Bi by paper chromatography..... Warren and Fink.

Procedure No. 7. Separation of carrier-free RaD(Pb^{210}) from micro amounts of Pb and Bi and macro amounts of Hg and Au using cellulose column chromatography.....Fink, et.al.

Procedure No. 8. Anion column separation of carrier-free RaD(Pb^{210}), RaE(Bi^{210}) and RaF(Po^{210}).....Hyde and Raby.

C. Separation of lead from cyclotron targets and complex mixtures.

Procedure No. 9. Preparation and isolation of carrier-free Pb^{203} from thallium.....Haymond, et.al.

Procedure No. 10. Separation of lead from thallium cyclotron targets.....Karraker.

Procedure No. 11. Separation of lead from mixed fission products.....Anon.

Procedure No. 12. Separation of lead from mixed fission products.....Osborne.

Procedure No. 13. Separation of lead from complex mixtures by controlled potential analysis.....Lingane and Jones.

Procedure No. 14. Separation of lead from neutron-activated samples of stoney meteorites.....Reed, et.al.

Procedure No. 15. Separation of carrier-free lead from organic materials.....Anon.

Procedure No. 1

Separation of short-lived carrier-free lead isotopes from bismuth parents.

From: R. Stockendal, J. A. McDonell, M. Schmorak and I. Berström, Arkiv für Fysik 11, 165 (1956).

Bismuth parents ($Bi^{199,201,203,205}$) produced by bombardment of natural lead with 25 Mev deuterons or protons of up to 70 Mev energy.

1. Dissolve lead target in concentrated nitric acid.
2. Add hydrochloric acid, and cool solution in an ice bath.
3. Separate the $PbCl_2$ precipitate by centrifugation and decant supernatent liquid into a clean tube.
4. Boil solution with addition of concentrated hydrochloric acid until nitric acid is completely destroyed, and evaporate to a small volume.
5. Dilute with water until the hydrochloric acid concentration is $\sim$ 0.3 M.
6. Pass through a jacketed column, heated to 82.3° by refluxing isopropyl alcohol and packed with Dowex-1

anion exchange resin, 200 mesh. Wash column with 0.3 M hydrochloric acid.

7. The bismuth isotopes are retained firmly on the resin, the lead is removed. After a suitable growth period, lead daughters can now be separated from the bismuth by rapidly passing 0.3 M hydrochloric acid through the column, under pressure and collecting it in a suitable container for counting.

Reviewer's Notes:

1- This separation or variants have been widely used to study short-lived lead isotopes. The method does not have general applicability but is included as being illustrative of the general class of milking experiments.

2- At slower column flow rates than used here, it is not necessary to heat the column above room temperature. Indeed, the bismuth is so firmly held by the resin it is not clear that heating is necessary in this case.

Procedure No. 2

Precipitation separation of lead from bismuth parent activity.

Procedure 82-2 from W. W. Meinke "Chemical Procedures Used in Bombardment Work at Berkeley", UCRL-432 (August 30, 1949). Procedure by: Neumann; Time for sepn: 5 min for separation, 15 min for purification; Yield: ~ 85%; Degree of Purification: <0.05% Bi contamination.

Bi purified, final step being precipitation as BiOCl (obtainable by method listed in steps 1-3).

Procedure 2 (Continued)

1. Dissolve in few drops conc. HNO_3. Add 10 mg Pb carrier (preferably $Pb(NO_3)_2$). Add 3 drops conc. HCl. Dilute to ~ 8 ml.
2. Add NH_3 dropwise until permanent precipitate just forms, and then HNO_3 dropwise until solution just clears.
3. At desired time for milking, dilute to 45 ml and heat in a water bath for a few minutes. Fine crystals of BiOCl should form. Centrifuge, and retain BiOCl for future milkings.
4. To the supernatent add a drop of NH_3. If the solution remains clear you have obtained a good separation.
5. Add 2-3 ml of $Na_2Cr_2O_7$ solution to cause precipitation of $PbCrO_4$. Centrifuge, and discard supernatent.
6. Dissolve $PbCrO_4$ by addition of 2 ml 4 N HCl and one drop 30% H_2O_2. Heat in water bath to destroy excess H_2O_2.
7. Add 20 mg inactive Bi carrier and repeat BiOCl separation by above method. Repeat precipitation of $PbCrO_4$.
8. Dissolve $PbCrO_4$ as in step (6).
9. Dilute to any desired volume and mount aliquots for counting. The results are reproducible and chemical yield determinations are not necessary. If the latter are desired, proceed with step (10).
10. Add 5 ml conc. H_2SO_4. Evaporate to fumes of SO_3. Resulting volume will be 2-3 ml. Cool. Dilute carefully to ~ 40 ml. Cool. Filter, dry and weigh $PbSO_4$.

Remarks:

Any single precipitation of BiOCl under these conditions gives a yield of 98-99% Bi, with 8% of the Pb retained with the Bi. One Bi scavange of the separated Pb should be sufficient purification from the parent.

Procedure 2 (Continued)

In calculating the life of the parent from consecutive milkings of the same Bi solution, correction should be made for the 8% of the daughter retained with the parent.

Purification of Pb as $PbSO_4$, gives varying yields, and determination of chemical yield by weighing is necessary.

Where the Pb fractions will be further milked for Tl, stop at step (8).

Procedure No. 3

Separation of lead from polonium parent activity.

Procedure 82-3 from W. W. Meinke "Chemical Procedures Used in Bombardment Work at Berkeley", UCRL-432 (August 30, 1949).

Procedure by: Karraker; Parent material: milking experiment from polonium parent; Time for sepn.: 5 min; Yield: 95-100%; Degree of purification: factor of 10^6 from Po with two washes.

Po is in 20% tributyl phosphate in dibutyl ether. To milk solution:

1. Extract with equal volume of 6 N HCl. Pb and Bi go into water phase.
2. Wash HCl extract twice with 1/10 its volume of tributyl phosphate solvent. Add the first portion to the Po solution, then discard second portion.
3. Add 1/2 mg Bi and 1/2 mg Pb carrier, (ppn made from $\sim$ 4 cc volumes).
4. To separate Bi and Pb, follow the procedure of Neumann (Procedure No. 2).
5. Thallium daughters of lead may be separated by oxidation with $KMnO_4$ and extraction of Tl^{+3} into ether.

Procedure No. 4

Separation of Pb^{210}(RaD) from old radon ampules by dithizone extraction.

From G. Bouissieres and C. Ferradini, Anal. Chim. Acta 4, 610 (1950).

1. Remove the radioactive RaD deposit by washing the ampules with hot concentrated nitric acid. If the dissolution of RaD is incomplete give the ampules a short treatment with a nitric acid-hydrofluoric acid mixture.
2. Evaporate the resultant solution until a light precipitate is obtained and redissolve by diluting the solution with a minimum amount of nitric acid. A small amount of undissolved silica will not interfere.
3. If the solution contains mercury add a small amount of potassium cyanide to complex this species.
4. Neutralize the solution to pH 9 with ammonium hydroxide and extract the lead with a solution of dithizone in chloroform (0.1g/ℓ) repeating the extraction until the chloroform fraction ceases to show the characteristic red color of lead dithizonate.
5. Agitate the dithizone with 0.1 N nitric acid. Remove the aqueous phase and repeat the extraction combining the nitric acid washes and discarding the chloroform phase.

Reviewer's Note:

This method will remove the lead from radium, mercury and other common contaminants of RaD deposits but will not provide separation from bismuth (RaE).

Procedure No. 5

Electrolytic separation of Bi^{212}(ThC) and Pb^{212}(ThB) from thorium nitrate.

From A. D. R. Harrison, A. J. Lindsey and R. Phillips, Anal. Chim. Acta 13, 459 (1955).

From an "old sample" of thorium nitrate (one in which the thorium daughters are in equilibrium), 1 gram is weighed out and dissolved in 20 to 25 ml 0.5 N hydrochloric acid. The requisite amount of standard bismuth solution (> 0.2 mg) is pipetted into the electrolysis solution which is heated in a water bath to 80-90°C. Clean platinum electrodes and a calomel half-cell are inserted and the electrolyzing current and a mechanical stirrer are switched on. The current is increased until a potential of 0.25-0.30 volts relative to the saturated calomel electrode is attained and the plating is continued for 25 minutes.

At the end of the deposition time, the cathode with the deposit of Bi^{212}(ThC) is withdrawn while the current was still on, washed with distilled water and alcohol and dried.

A fresh cathode is then introduced into the electrolysis cell, the current is increased to about 0.15 amps/cm^2 with no controlled potential being employed and the electrodeposition continued for 10-20 minutes. The cathode is again removed with the current left on, rinsed with water and alcohol, dried, and counted directly.

Procedure No. 6

Rapid separation of carrier-free RaD(Pb^{210}) from Pt, Au, Po and Bi by paper chromatography.

Decontamination factor > 10^6.

From G. W. Warren and R. W. Fink, Department of Chemistry, University of Arkansas, Fayetteville, Arkansas.

Chemicals:

n-butyl phosphate, C.P.; acetone, C.P.; Eaton-Dikeman Grade 320; industrial paper, 0.1 or 0.06 in. thick.

Equipment:

Glass tube with minimum dimensions: diameter, $\geq$ 2 inches; height $\geq$ 12 inches.

1. The glass tube is placed erect in a beaker containing 80% acetone-20% n-butyl phosphate and the top sealed with a cork or rubber stopper fitted with a glass hook to serve as the 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 concentrations not greater than 5 x 10^{-5} grams per cm 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 of 10 cm width of paper.
5. Apply the solution evenly across the width of the paper strip (see Note 1) about 3 cm from the end with a micro-pipet.
6. Suspend the strip from the glass hook so that the end

of the paper is just immersed in the developer. Separations are obtained after the solvent front has travelled 5-6 inches (10-15 minutes).

7. Remove the paper strip and identify the various zones. The normal R values (the ratio of the distance travelled by a component to the distance travelled by the solvent front are: Au^{3+} = 1.0; Hg^{2+} = 0.90; Po^{4+} = 0.80; Pt(IV) = 0.5; Tl^{3+} = 0.05; Bi^{3+} = 0.60; Pb^{2+} = 0.00.
8. The desired zones are clipped from the strip and the cations extracted by boiling with aqua regia or extracted with an organic solvent for subsequent mounting and counting.

Notes: 1- The Eaton-Dikeman Grade 320 Industrial Paper was purified by downward percolation with 1 N hydrochloric acid and rinsed by downward percolation with water.

Notes: 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. The 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 6 (Continued)

Remarks:

This technique affords a simple and fast separation method with exceptionally high mutual decontamination factors. The time for separation is less than 15 minutes. Improper paper purification, impure reagents, or excess carrier concentration may cause poor separations.

Procedure No. 7

Separation of carrier-free RaD(Pb^{210}) from micro amounts of Po and Bi and macro amounts of Hg and Au using cellulose column chromatography.

From R. W. Fink, G. W. Warren, R. R. Edwards and R. E. Damon, Phys. Rev. 103, 651 (1956).

Material;old radion seeds in the form of gold needles containing appreciable amounts of mercury.

1. In a column 17 mm in diameter and 80 cm long, slurry Whatman No. 1 ashless cellulose powder with the eluent to be used (n-butanol saturated with 3 N hydrochloric acid) and pour onto the column.
2. Flow eluent through the column overnight to pack the cellulose powder to a depth of ~ 40 cm.
3. Make the RaDEF solution containing gold and mercury 3 N in hydrochloric acid add n-butanol saturated with 3 N hydrochloric acid, a small amount of the cellulose powder and mix thoroughly.
4. Pour the slurry on top of the previously prepared cellulose column.
5. After the loading solution has passed into the column and the slurried powder has settled, put n-butanol saturated

with 3 N hydrochloric acid on top of the column. The first two additions should be in small amount (~ 5 ml).

6. Collect the fractions. Gold, mercury and polonium (RaF) come off quantitatively in a narrow band after one column volume of eluant is passed through the column. Carrier-free bismuth (RaE) comes off about two column volumes later. One or two column volumes later carrier-free lead (RaD) is eluted.

Note: Entire procedure requires about 90 minutes. If macro-quantities of gold and mercury are absent the faster method of Warren and Fink (Procedure No. 6) can be used.

Procedure No. 8

Anion column separation of carrier-free Pb^{210}(RaD), Bi^{210}(RaE) and Po^{210}(RaF).

Adapted from B. A. Raby and E. K. Hyde, U.S. Atomic Energy Commission Declassified Document AECD-3524 (1952); also University of California Radiation Laboratory Report UCRL-2069 (1952).

1. In a 3mm diameter glass tube constricted at the bottom and containing a glass-wool plug, add a slurry of Dowex-A-1 anion exchange resin (50-100 mesh) to a final resin depth of 20 mm. Convert resin to chloride form by passing concentrated hydrochloric acid through the resin; then wash the resin with 1-2 M hydrochloric acid.
2. Put tracer Pb, Bi, Po onto the column in 2ml of 1 M hydrochloric acid. Pass 3 ml of 1 M hydrochloric acid in 1 ml portions. Collect loading and wash eluants since this

contains the lead which is not adsorbed by the resin at this concentration.

3. Pass 4 ml concentrated hydrochloric acid through the column in 2 ml portions to remove the bismuth.
4. The polonium can then be removed with 4 ml concentrated nitric acid.

Notes: 1- The decontamination factors for this procedure are very good but may vary from one resin batch to another.

2- The separations can be effected in 10-15 minutes and the products are obtained in carrier-free form.

Procedure No. 9

Preparation and isolation of carrier-free Pb^{203} from thallium.

From H. R. Haymond, W. M. Garrison and J. G. Hamilton, "Carrier-Free Radioisotopes from Cyclotron Targets XXII. Preparation and Isolation of Pb^{203} from Thallium", University of California Radiation Laboratory Report UCRL-1421 (July 18, 1951).

The 52-hour Pb^{203} was produced by the reaction Tl^{203} (d,2n)Pb^{203}. The target consisted of a 2 mm layer of Tl_2O_3 powder held on a grooved water-cooled copper plate by a 0.25 mil platinum foil and was bombarded with 19 Mev deuterons. The beam current was limited to 5 ua to avoid volatilization of the target powder during bombardment.

1. Dissolve the Tl_2O_3 target powder in 1 N NHO_3.
2. Saturate solution with SO_2 gas to reduce the Tl to Tl^{+1} and heat solution to expel excess SO_2.

Procedure 9 (Continued)

3. Add 10 mg of Fe^{+++} carrier and make the solution basic with NH_4OH. Centrifuge $Fe(OH)_3$ precipitate and discard supernatent solution.
4. Wash the $Fe(OH)_3$ precipitate twice in dilute NH_4OH solution with stirring, centrifuge and discard; wash solution each time. Dissolve precipitate in 1 N HNO_3.
5. Add 5 mg of Tl^{+3} carrier and repeat steps 2-4.
6. Repeat steps 2-4 once more without addition of thallium carrier and dissolve the final $Fe(OH)_3$ precipitate in 6 N HCl instead of 1 N HNO_3.
7. Remove the iron by four extractions with equal volumes of ethyl ether. The final aqueous solution contains the carrier-free lead-203 which can then be put in the proper form for biological, chemical or physical tracer experiments.

Remarks: The 68 minute Pb^{204} which results from deuteron bombardment of Tl was allowed to decay out prior to the separation.

The decay curve, over four half-lives, and the absorption curves indicated only the presence of lead-203 in the final product.

Procedure No. 10

Separation of lead from thallium cyclotron targets.

Procedure 82-1 from W. Meinke "Chemical Procedures Used in Bombardment Work at Berkeley", UCRL-432 (August 30, 1949).

Procedure by: Karraker; Target Material: thallium; Type of bbdt: 60-80 Mev D^+ or H^+; Time for sepn.: ~ 1 hour; Yield: ~ 95%; Degree of purification: good, at least factor of 100; Advantages: one step is usually sufficient purification.

Procedure 10 (Continued)

1. Dissolve Tl target in 6 M H_2SO_4, the smallest amount possible. Add 5 mg Pb carrier, also 5 mg Hg carrier as hold-back.
2. Evaporate solution over a hot plate, with air-jet blowing on the top of the solution, till fumes of SO_2 appear and the solution is quite concentrated.
3. Dilute carefully with 2 volumes of H_2O. $PbSO_4$, white ppt, appears. Wash ppt. with 2 M H_2SO_4, then with H_2O. If desired, this may be dissolved in NH_4Ac and repptd as $PbCrO_4$. However, it is usually sufficiently pure without further steps.

Remarks: Add conc. H_2SO_4 to water, not water to acid!!

Procedure No. 11

Separation of lead from mixed fission products.

Author unknown. This procedure has been used for separation of low-level lead activity from high level mixed fission product sources (~ 5 day old samples of up to 10^{15} fissions) with negligible contamination of the lead fraction. The time required is about 4 hours, the chemical yield is 40-60 per cent.

1. To 20 mg. of lead carrier in a 40 ml centrifuge cone, add the solution containing the lead activity. If barium carrier is not present, add ~ 10 mg barium scavange. Boil the solution to dryness twice with hydrochloric acid.
2. Dilute to 10 ml with water (note a), precipitate PbS by saturating with H_2S gas, centrifuge and wash the

precipitate with water. Dissolve the PbS in one ml concentrated hydrochloric acid with heating, add one ml concentrated H_2SO_4, stir and dilute to 10 ml with water. Centrifuge $PbSO_4$ and wash with 5 ml water.

3. Dissolve the $PbSO_4$ ppt. in 4 ml 6 N NH_4Ac, add 20 mg Ba scavange with stirring and two drops of concentrated H_2SO_4 with stirring. Centrifuge the $BaSO_4$ precipitate at high speed. Wash the precipitate with 10 ml of 6 N NH_4Ac.
4. Dilute the combined supernate and wash solutions to 20 ml. with water, neutralize to methyl red end point with NH_4OH and saturate with H_2S. Centrifuge the PbS and wash with 10 ml H_2O.
5. Dissolve the PbS precipitate in 2 ml of concentrated nitric acid and boil until $Pb(NO_3)$ begins to settle out. Add 15 ml fuming HNO_3 and cool in an ice bath for 20 minutes. Centrifuge, dissolve the $Pb(NO_3)_2$ in 1-2 ml of water and repeat fuming nitric step.
6. Dissolve the $Pb(NO_3)_2$ in 1-2 ml water and add 10 mg Fe^{+++} scavange. Pour this into a tube containing 5 ml 6 N NaOH, with stirring. Heat solution to boiling and digest several minutes. Centrifuge $Fe(OH)_3$.
7. Neutralize the supernate to methyl red charge with HCl and NH_4OH (a white ppt results on slightly basic side), add one ml 6 N HAc (ppt dissolves) and 2 ml 6 N NH_4Ac. Place solution in a hot bath and add 2 ml 3 N Na_2CrO_4 solution. Digest for 10 minutes in a hot water bath.
8. Centrifuge the $PbCrO_4$ precipitate and wash with 10 ml water. Dissolve the lead chromate in 2 ml concentrated nitric acid and boil until $Pb(NO_3)_2$ salts out.

9. Dilute to 2-3 ml with water, add 1 ml concentrated sulfuric acid and boil until SO_3 fumes are given off (note b). Add 10 ml water and heat the solution for a few minutes, stirring thoroughly. Centrifuge the $PbSO_4$ and wash with 10 ml of a 1:1 EtOH-H_2O mixture. The time of precipitation of $PbSO_4$ is the final separation from bismuth.
10. Filter the $PbSO_4$ onto a previously tared Whatman No. 42 filter paper disc. Wash the $PbSO_4$ with two 5 ml portions of ethanol. Dry the filter paper in an oven for ten minutes and weigh to a constant weight (gravimetric factor 0.68325).

Reviewer's Notes:

a- The HCl concentration should be less than 0.5 N in order to get complete precipitation of the lead sulfide.

b- Do not fume excessively because this produces anhydrous $Cr_2(SO_4)_3$ which is insoluble in water.

Procedure No. 12

Separation of lead from mixed fission products.

From M. Lindner "Radiochemical Procedures in Use at the University of California Radiation Laboratory (Livermore)", UCRL-4377 (August 10, 1954).

Procedure by: R. N. Osborne; Purification: 10^{10} atoms of Pb^{203} isolated from a 7 day old fission mixture containing 10^{15} fissions showed no evidence of foreign radioactivity over six half-lives; Yield: about 50 per cent; Separation time: app. four hours.

Procedure 12 (Continued)

1. To the active solution add a lead carrier solution containing 10 mg Pb. Add 2 ml conc. H_2SO_4 and boil to fumes of H_2SO_4. (Note: If this initial isolation step is not applicable, an alternative procedure might involve the precipitation of lead sulfide from an ammoniacal tartarate solution.) Cool, cautiously add water, stir, centrifuge, and wash the $PbSO_4$ with 1 N H_2SO_4.
2. Dissolve the $PbSO_4$ in ~ 2 ml 6 N NH_4Ac. Dilute to 10 ml with H_2O, saturate with H_2S and centrifuge the PbS.
3. Dissolve the PbS in ~ 5 ml conc. HCl and pass solution through an anion column (Dowex 1 x 8, 50-100 mesh) that has been washed with conc. HCl. Wash through column with ~ 6 ml conc. HCl. Combine eluate with wash and boil to near-dryness.
4. Add ~ 10 ml 2 N HCl and ~ 2 mg each of the following carriers: Cu, Bi, Pd, Ag and Te. Saturate with H_2S and centrifuge. Discard precipitate.
5. Boil the supernatant to expel the H_2S and add ~ 2 mg Fe and La carriers. Add NaOH until the solution is basic. Centrifuge and discard precipitate.
6. Add ~ 1 ml conc. H_2SO_4 and ~ 2 mg Ba and Sr to the supernatant, and boil to fumes of H_2SO_4. Cool and dilute to ~ 10 ml with water. Centrifuge and discard supernatant.
7. Wash the precipitate with 5 ml water. Leach the Pb from the combined sulfates with 2 ml portions 6 N NH_4Ac (heat). Centrifuge and discard remaining precipitate.
8. Add ~ 10 ml water to the solution and saturate with H_2S. Centrifuge and discard supernatant.
9. Dissolve the precipitate in conc. HCl, boil to near-

dryness and add ~ 10 ml 2 N HCl and ~ 2 mg of the following carriers: Cu, Bi, Pd, Ag and Te. Saturate with H_2S, centrifuge and discard precipitate.

10. Boil the supernatant to expel the H_2S and add ~ 2 mg Fe and La carriers and ~ 0.5 gram of NH_4Cl. Make basic with NH_4OH. Centrifuge and discard precipitate.
11. Saturate the supernate with H_2S. Centrifuge and discard supernatant.
12. Dissolve the precipitate in ~ 1 ml conc. HNO_3, add ~ 10 ml fuming HNO_3, and chill in an ice bath.
13. Dissolve the precipitate in ~ 2 ml water. Add ~ 1 ml conc. H_2SO_4. Boil to fumes of H_2SO_4, cool and add ~ 10 ml water and 5 ml EtOH.
14. Wash the precipitate once with ~ 5 ml water, once with a mixture of ~ 5 ml water and ~ 5 ml EtOH and twice with ~ 5 ml portions of EtOH.
15. Slurry the precipitate onto an aluminum plate and dry under a heat lamp. Weigh as $PbSO_4$.

Procedure No. 13

Separation of lead from complex mixtures by controlled potential electrolysis.

From: I. J. Lingane and S. S. Jones, Anal. Chem. 1789 (1951).

Depositions are performed onto a clean platinum cathode from a 0.25 M tartarate solution of pH 5.8-6.0 containing 1 gm hydrazine hydrochloride per 100 ml. The cathode can be changed between depositions. The depositions can be sequentially performed at the following voltages: Cu, -0.30 v; Bi, -0.40 v;

Pb, 0.60 v. If only lead separation is required a prior deposition at -0.40 volts should be carried out.

Reviewers Note: A small amount of lead and bismuth carrier must be present. The amount of lead 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 constant value.

Procedure No. 14

Separation of lead from neutron-activated samples of stony meteorites.

From: G. W. Reed, K. Kigoshi and A. Turkevich, Proceedings of the 2nd U.N. Conference on Peaceful Uses of Atomic Energy 28, 486 (1958).

A. Preliminary treatment and irradiation

One to two gram samples of the meteorite were placed in quartz vials and irradiated in a reactor for two to three days in a neutron flux of 5×10^{13} neutrons cm^{-2} sec^{-1}.

B. Separation procedure

After irradiation, the meteorite samples were placed in nickel crucibles containing 2 mg lead carrier and about 10 grams of sodium peroxide was added. The mixture was then fused. The fused mass (after cooling) was broken up with water and removed from the crucible. The mixture was then acidified and a clear solution was obtained. After making the solution 0.5 M in hydrochloric acid, 200 mg of strontium was added and lead and strontium sulfates were precipitated with ammonium sulfate.

The lead was decontaminated by converting the sulfate to carbonate, dissolving in hydrochloric acid, and then repeating

cycles of acid sulfide precipitations, sulfate precipitations and dithizone extractions. The lead was finally electrodeposited on a platinum disc. The chemical recovery of lead was about 50 per cent.

Radioactive measurement

The irradiated samples showed about one curie of radiation six hours after removal from the pile. The amount of lead activity in the separated sample was usually in the range 10-100 disintegrations per minute. The radioactivity was measured with thin end window atomospheric pressure porportional counters operating with pure methane at about 4000 volts. The counting efficiency was close to 50 per cent for Pb^{209} but only 5-10% for Pb^{203} which decays by K-electron capture.

Procedure No. 15

Separation of lead in carrier-free form from organic materials.

From a report prepared by the Metallic Impurities in Organic Matter Sub-Committee of the Analytical Methods Committee on the Determination of Lead. Reported in Analyst 84, 127 (1959).

Principle of method-

After removal of interfering substances, lead is extracted with dithizone at pH 9 to 9.5.

For the preliminary separation of lead, two methods are given. In Method A, lead is extracted with dithizone from an alkaline citrate and hexametaphosphate solution.

Method B requires additional manipulation and should be used only when Method A will not suffice, i.e.: for samples

with a high content of calcium, magnesium and phosphate.

If bismuth interference is indicated, the modified procedure given under "Interference of Bismuth" should be used.

If carrier-free samples are required, then special care must be taken with purity of reagents and lead-free borosilicate glass or silica should be used throughout.

Reagents- (If method B or the special bismuth separation is not needed only those marked with an asterisk are needed.)

Hydrochloric Acid, concentrated

Hydrochloric Acid, 5 M

Nitric Acid*, dilute (1:100)

Sulfuric Acid, diluted 1:1

Perchloric Acid, sp. gr. 1.54

Ammonium hydroxide*,

Ammonium citrate solution* 25% w/v in water

Sodium hexametaphosphate solution*, 10% w/v in water

Sodium iodide solution, 20% w/v in water

Sodium metabisulfite solution, 1.25% w/v in water. Prepare this solution freshly as required, and filter before use.

Potassium cyanide solution* 10% w/v in water. This solution should be at least 2 days old, so that traces of sulfide are oxidized.

Hydroxylamine hydrochloride solution*, 20% w/v in water

Chloroform*, shake 250 ml of chloroform with 25 ml of water containing 1 ml of 10% KI soln and about 20 drops of 5 M NH_4OH, separate and reject the aqueous layer, wash the chloroform with water and filter.

Dithizone, stock solution*, 0.1% dithizone in chloroform

Dithizone, working solution*, shake 6 ml of dithizone stock solution with 9 ml of water and 1 ml 5 M NH_4OH. Separate and reject lower layer. Prepare on day of use.

Diethylammonium diethyldithiocarbamate solution, 1 per cent (carbamate reagent). Dissolve 1 g of pure crystalline reagent in 100 ml of redistilled chloroform and store in dark bottle. This solution should be discarded after 1 week.

Methyl red indicator solution, 0.01 per cent. Warm 25 mg methyl red with 0.95 ml 0.05 M NaOH and 5 ml of 90% ethanol. When dissolution is complete add 50% ethanol to 250 ml.

Thymol blue indicator solution*, 0.04%. Warm 0.1 g of thymol blue with 4.3 ml 0.05 M NaOH and 5 ml 90% ethanol. Add 20% ethanol to 250 ml.

Procedure-

A. Destruction of organic matter

Destroy the organic matter in a measured amount of sample by a suitable procedure, such as:

1. Dry ashing at temperature not exceeding 500°C.
2. Oxidation with nitric and perchloric acids.
3. Oxidation with nitric and sulfuric acids (to be avoided if large amounts of calcium are present or suspected).

B. Preliminary treatment of sample

1. If the organic matter has been destroyed by wet decomposition, allow the flask to cool and add 5 ml water. Filter the solution and washings into a 100 ml conical flask. Treat any residue with boiling 5 M hydrochloric acid and filter into same flask.
2. If the organic matter has been destroyed by dry ashing add 5 ml water and 10 ml 5 M HCl to the ashing dish and boil gently for 5 minutes, filter supernatent liquid and washings into 100 ml conical flask.

C. Separation of lead. Method A (for samples low in Ca, Mg and phosphate).

1. Cool the soln, add 5 ml of ammonium citrate solution and

Procedure 15 (Continued)

10 ml sodium hexametaphosphate soln.

2. Add a few drops of thymol blue indicator and NH_4OH to give blue-green color indicating pH 9.0-9.5.
3. Cool, add 1 ml potassium cyanide solution, 1 ml hydroxylamine hydrochloride solution and transfer to a 100 ml seperatory funnel containing 10 ml of chloroform. Rinse with a few ml water. The volume of the aqueous layer should be about 50 ml.
4. Add 0.5 ml of dithizone working solution, shake for one minute and allow to separate. If the lower layer is red, add dithizone working solution until, after shaking, a purple, green or blue color is obtained.
5. Run the chloroform layer into a second seperatory funnel, and wash through with 1 or 2 ml of chloroform.
6. Add to the liquid in the first seperatory funnel 3 ml of chloroform and 0.2 ml of dithizone working solution. Shake for 30 seconds and add chloroform layer to first chloroform extract. Continue extractions until the chloroform extract is green. Reject the aqueous layer.
7. Shake 2-10 ml portions 5 M hydrochloric acid to which 1 ml ammonium citrate and 2 ml sodium hexametaphosphate solutions have been added and the pH adjusted to 9-9.5 followed by addition of a few drops of potassium cyamide solution with the chloroform extract, rejecting the aqueous layer as completely as possible each time (step added by reviewer).
8. Add 10 ml of dilute nitric acid to the chloroform extract. Shake vigorously for 1 minute and reject the chloroform layer as completely as possible. Add 5 ml chloroform to the aqueous solution, shake and again reject the chloroform layer.

9. Carrier-free lead is now in the nitric acid solution and can be mounted and counted as desired.

D. Separation of lead, Method B(for samples containing large amounts of Ca, Mg and phosphates)

1. To the solution obtained by one of the methods described under B "Preliminary treatment of sample" add 2 drops of methyl red indicator and make just alkaline with NH_4OH.
2. Make the solution just acid with 5 M hydrochloric acid and add a further 10 ml. Warm the solution to 50-70°, add 2 ml sodium iodide solution and reduce any liberated iodine with 2 ml of sodium metabisulfite solution.
3. Cool the solution, transfer to a seperatory funnel and adjust the volume to 50-75 ml (in order to make the acid concentrations ~ 1 M).
4. Add 10 ml of carbamate reagent and shake for 30 seconds. Transfer the chloroform layer to a 100 ml flask. Wash the aqueous layer twice with small amounts of chloroform without shaking and add washings to the flask.
5. Repeat the extraction with 10 ml of carbamate reagent, add to first extract. Reject aqueous layer.
6. To the combined extracts add 2.0 ml of diluted sulfuric acid, and evaporate the chloroform. Add 0.5 ml of perchloric acid and heat until fumes are evolved and solution is clear and colorless.
7. Cool, add 10 ml of water and 5 ml of 5 M hydrochloric acid. Boil for 1 minute, cool and add 2 ml of ammonium citrate solution.
8. Continue as in Method A beginning at step 2.

E. Separation from bismuth (unnecessary unless presence of bismuth is known or suspected).

1. Prepare the digest from the wet decomposition or the dry

ashing as in B. Place solution into a 50 ml graduated seperatory funnel and adjust such that final volume is ~ 35 ml with a total acid concentration of 6 N of which at least 3 N is hydrochloric acid. For example the concentration can be 3 N hydrochloric and 3 N sulfuric acid (as from wet digestion using sulfuric acid) or 6 N hydrochloric acid (as from dry ashing followed by hydrochloric acid leach).

2. Extract the acid solution directly in the cold, first with 10 ml and then with 5 ml of carbamate reagent shaking for 30 seconds each time. Separate and discard the lower (chloroform) layer. Finally shake the acid with 5 ml of chloroform and discard the chloroform.
3. Transfer the acid layer to a 100 ml conical flask and proceed as in Method A or Method B above.

Reviewers Note: This procedure was not specifically developed for separation of radioisotopes of lead but should be directly applicable in almost all respects. It demonstrates procedures used with organic substances and also shows the use of dithizone extraction separation which is applicable also to inorganic materials.

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