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The Radiochemistry of Polonium

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CHEMISTRY

The Radiochemistry of Polonium

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January 1961

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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FOREWORD

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

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

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

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

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

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of polonium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of polonium which might be included in a revised version of the monograph.

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I. GENERAL REVIEWS OF THE CHEMISTRY AND RADIOCHEMISTRY OF POLONIUM

(1) "Chemistry of the Rare Radioelements" by K. W. Bagnall, pp. 1-94, Academic Press Inc., New York, 1957, 348 references (This comprehensive review covers the literature up to 1956. Since a literature search of the early work on Po would only duplicate material published in this book, extensive use has been made of the material cited in this review. The author wishes to acknowledge his indebtedness to this source.)

(2) "Polonium" ed. by H. V. Moyer, U. S. Atomic Energy Commission TID-5221, 381 pp. 1956 (A summary of the work on Po performed at Mound Laboratory)

(3) Gmelin Handbuch der anorganischen Chemie, System Number 12, Verlag Chemie, G.m.b.H., Berlin, 1941 (A comprehensive review of the early Po work.)

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*Operated by Monsanto Research Corporation, Miamisburg, Ohio.

(4) "Le Polonium, Act. Sci. 517" by M. Haissinsky, Hermann et Cie., Paris, 1937

(5) "Electrochimie des Substances radio-actives, Act. Sci. 1009" by M. Haissinsky, Hermann et Cie., Paris, 1946

(6) "Some Aspects of Polonium Chemistry" by K. W. Bagnall, Proc. Int. Conf., Geneva, 1955, 7, pp. 386-388, U.N., New York, 1956. 29 references.

(7) "Chemistry of Polonium" by K. W. Bagnall, Quart. Rev., 11, 30-48, (1957). 79 references.

(8) "Chemie des Poloniums" by F. Weigel, Angew. Chemie, 71, 289-299, 1959. 144 references.

II. TABLE OF ISOTOPES

Isotope	Half-Life	Decay	Energy of Radiations (Mev.)	Method of Preparation
Po^{196}	1.9 m	α	6.14	
Po^{197}	4 m	α	6.040	
Po^{198}	6 m	α	5.935	
Po^{199}	11 m	α	5.846	
Po^{200}	11 m	EC α	5.770	
Po^{201}	18 m	EC α	5.671	
Po^{202}	51 m	98% EC 2% α	5.575	Daughter of Rn^{206}
Po^{203}	42 m	EC		
Po^{204}	3.8 h	99% EC 1% α	5.370	Daughter of Rn^{208} Daughter of At^{204}
Po^{205}	1.8 h	99+% EC 074% α	5.2	Daughter of At^{205} $Pb^{204}(\alpha,3n)$
Po^{206}	8.8 d	95% EC 5% α γ	5.218	Daughter of Rn^{210} Daughter of At^{206}
Po^{207}	5.7 h	99+% EC 10^{-2}% α γ	5.10	$Pb^{206}(\alpha,3n)$
Po^{208}	2.897 y*	α EC γ	5.108	$Pb^{207}(\alpha,3n)$ $Bi^{209}(p,2n)$ $Bi^{209}(d,3n)$

* K. C. Jordan, Private communication.

Isotope	Half-Life	Decay	Energy of Radiations (Mev.)	Method of Preparation
Po^{209}	103 y	99+% α 0.5% EC γ	4.877	Bi^{209} (p,n) Bi^{209} (d,2n) Daughter of At^{209}
Po^{210} (RaF)	138.401 d	99+% α 10^{-3}% α	5.305 4.5	Bi^{209}(n,γ)Bi^{210} $\xrightarrow{\beta^-}$ Po^{210} Daughter of Bi^{210}(RaE)
Po^{211m}	25 s	α	7.14 7.85 8.70	
Po^{211} (AcC')	0.52 s	α	7.442	Daughter of Bi^{211}
Po^{212} (ThC')	3×10^{-7} s	α	8.780	Daughter of Bi^{212}
Po^{213}	4.2×10^{-6} s	α	8.35	Daughter of Bi^{213} Daughter of Rn^{217}
Po^{214} (RaC')	1.64×10^{-4} s	α	7.680	Daughter of Bi^{214}
Po^{215} (AcA)	1.83×10^{-3} s	α	7.36	Daughter of Rn^{219} Daughter of Bi^{215}
Po^{216} (ThA)	0.158 s	α	6.775	Daughter of Rn^{220}
Po^{217}	10 s	α	6.54	Daughter of Rn^{221}
Po^{218} (RaA)	3.05 m	α	5.998	Daughter of Rn^{222}

For more complete information on the radiations of the polonium isotopes and for references to 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.

III. REVIEW OF THOSE FEATURES OF POLONIUM CHEMISTRY OF CHIEF INTEREST TO THE RADIOCHEMIST.

1. General

Polonium was discovered by Pierre and Marie Curie in 1898 in the course of research on the radioactivity of uranium and thorium minerals. They found that Po behaved similarly to Bi and subsequently were able to separate it from Bi by vacuum sublimation.

The earliest work on Po was complicated by the extremely small quantities available and sometimes by incomplete separation of radioactive impurities, so that it was not until 1906 that the identification of Po was definitely established. Until 1944, with one exception[1], all of the work on Po was conducted on the trace level. While most of the results were valid, a few erroneous conclusions were reached concerning the basic chemistry of Po. However, work with milligram quantities of Po during the last 15 years has placed the chemistry of Po on a sound basis.

Polonium-210 (RaF) occurs naturally in the uranium-radium decay chain. The equilibrium ratio of U to Po is 1.19×10^{10}, so that the Po concentration in uranium ores is less than 0.1 mg/ton. The lead fraction of residues from uranium processing (RaDEF) offers a more concentrated source of Po^{210}, but the concentration of Po is still less than one mg/ton. Polonium-210 can also be obtained from aged Ra salts (0.2 mg of Po per gm of Ra at equilibrium) and from aged Rn tubes. With the advent of nuclear reactors and their intense neutron fluxes, the reaction

$_{83}Bi^{209}$ (n,γ) $_{83}Bi^{210} \xrightarrow[5\,d]{\beta^-} {}_{84}Po^{210}$ has become economically feasible. This process is currently used for the production of milligram quantities of Po.

A number of other isotopes of Po also appear in natural occurring decay series. However, the short half-lives of all preclude any appreciable concentration of these isotopes in nature. Polonium-213 is a member of the artificially produced 4n+1 series, but its half-life is also short.

One of the difficulties of working with Po^{210} is its high specific activity (0.2222 mg/c). The intense radiation of milligram samples quickly decomposes most organic complexing agents and even the solvents. Crystal structures of solids are quickly destroyed or altered. For this reason it would be desirable to work with an isotope of lower specific activity. The use of Po^{209}, with a half-life of 103 yr., would reduce radiation effects about 600-fold. $Polonium^{209}$ can be formed by bombarding Bi^{209} with protons in a cyclotron;[2] however, much more Po^{208} ($t_{1/2}$ = 3 yr) is produced than Po^{209}. A sample of Po^{208}-Po^{209} was prepared by Oak Ridge National Laboratory and purified at Mound Laboratory.[3,4] The total sample contained about one curie of activity and it was estimated that the sample contained 14.5% by weight of Po^{209} relative to the total Po content.[3] This sample was used for spectroscopic measurements[4] and determination of the gamma spectrum of Po^{209}.[3]

The handling of Po requires special precautions. Since the maximum permissible body burden for ingested Po is only 0.02 μc

(4.5×10^{-12} g of Po^{210}) safety precautions must be vigorously observed. Low level sources, of the order of a few millicuries, can be handled as solutions with reasonable safety in fume hoods under an adequate draft, but it is inadvisable to handle dry sources, even at the millicurie level, in anything but sealed systems. Due to the volatility of some Po compounds (e.g. halides) and the high specific activity, a glovebox system is reccommended for μc amounts and over. For a more detailed discussion of the problems associated with high levels of Po see Reference 5, pp. 32-42.

2. Metallic Polonium

Polonium metal is silvery gray in color, and is soft enough to be scratched readily. The metal reacts slowly with O_2 at room temperature, but rapidly at elevated temperatures. Therefore, the pure metal should be stored under vacuum or in an inert atmosphere. The intense radiation of curie level samples causes a fluorescence in the surrounding gas and in glass or silica containers. In the dark, a quite spectacular blue-white glow is observed from curie level metallic samples or suspensions of insoluble Po compounds. The intense radiation of large samples of Po has a heating effect (27.4 cal/hr/curie-theoretical value),[5] so that the temperature of the sample can be well above its surroundings. The radiation also affects glass or silica containers, causing them to become dark and fragile(crazing).

Early measurements of the physical properties of Po were hampered by the small quantities of material available and by impurity of the samples. Table I lists some of the physical properties determined at Mound Laboratory with milligram level samples. X-ray powder photography indicates that the metal exists in at least two allotropic modifications: a low temperature α phase with a simple cubic lattice and a high temperature β phase, with a simple rhombohedral lattice. The phase change occurs at about 36°C, but the two phases may co-exist between 18 and 54°C.[7] Because of the heating effect of the alpha radiations, freshly prepared Po metal exists in the β phase. As the Po decays, the heating effect decreases, and the metal slowly converts to the α form.

TABLE I

PHYSICAL PROPERTIES OF POLONIUM METAL*

Density	Wt.-Vol. detn.	9.3 g/cm^3 (β phase)
	X-ray	α 9.196 g/cm^3 β 9.398 g/cm^3
Melting Point		252 ± 2°C
Boiling Point (extrapolated from vapor pressure data)		962.04 ± 1.93°C
Heat of Vaporization		24,597 ± 31 cal/mole

* Reference 6, pp. 21-26

The vapor pressure in the temperature range of 438 to 745°C has been measured,[8] and the derived vapor pressure equation is

$$\log P = \frac{-5377.8 \pm 6.7}{T} + 7.2345 \pm 0.0068$$

where T is the temperature in °K and P is the pressure in mm

Hg. This equation was then used to calculate the boiling point of Po.

The pure metal can be prepared in a number of ways. The earliest attempts involving sublimation in air yielded the oxide. However, sublimation in an inert atmosphere (H_2 or N_2) or vacuum sublimation onto quartz or glass produces the pure metal. Platinum and palladium as well as a number of other metals have been used to condense Po but polonide formation may occur in some cases. The metal has also been prepared in milligram amounts by cathodic deposition on platinum or gold. Spontaneous deposition on a less noble metal yields a metallic deposit, but often this is contaminated with Bi (RaE).

Probably the simplest method of obtaining milligram quantities of pure polonium is to precipitate the sulfide from dilute HCl. When the precipitate is heated to 500°C under vacuum, the sulfide decomposes and pure Po metal sublimes.[9,10] Procedure XII describes this method in detail.

3. Oxidation States

The electron configuration of neutral Po atoms in ground states is probably $5s^2 5p^6 5d^{10} 6s^2 6p^4$ ($^3P_2$) analogous to the configurations of Se and Te, from which stable oxidation states of -2, +2, +4, and +6 would be expected.

Polonides The existence of a -2 oxidation state was first suggested by the observation that when Po was melted with Ag or Cu, the Po could not be recovered quantitatively by distillation. If the Po was electroplated or volatilized onto these metals, no such difficulty was observed. Recently, a number of polonides have been prepared on the milligram scale and characterized. Polonides of Zn, Pb, Pt, Ni, Ag, Be, Ca, Na, Hg, and Mg have been reported.[5,6] The electrode potential for Po/Po^{-2} has been calculated to be -1.0 volt by extrapolation of the corresponding potentials of other Group 6B elements.[11]

Bivalent Polonium Bivalent Po chloride and bromide have been prepared on a milligram scale.[5] In solution these compounds are subject to oxidation by the products of the intense alpha bombardment, hereafter referred to as autooxidation. The monoxide and monosulfide have also been prepared, and both demonstrate the same tendency to autooxidize. A bivalent polonium sulfate has probably been prepared.[5]

Trivalent Polonium Much of the evidence for trivalent Po is based on coprecipitation experiments and is, therefore, subject to question. Some evidence indicates that trivalent Po may be an unstable intermediate in the autooxidation of bivalent Po.

Quadrivalent Polonium The +4 oxidation state is the stable state in solutions. The dioxide can be formed directly from the elements and forms spontaneously when the metal is exposed to air. The tetrachloride, tetrabromide and tetraiodide have been prepared and characterized. A number of complexes of the general formula M_2PoX_6 have been prepared where M is a singly charged cation and X is a halide. These and other quadrivalent Po compounds will be described in more detail in later sections.

Other quadrivalent Po compounds which have been prepared and characterized are the hydroxide ($PoO(OH)_2$), sulfate, nitrate and selenate. Less well characterized are the carbonate, chromate, phosphate, and vanadate.

Hexavalent Polonium A higher oxide, probably PoO_3, is considered to be the product obtained by the anodic deposition of trace Po. Chemical evidence tends to support this view.[12] Some evidence for a hexavalent state has also been observed from co-precipitation behavior.

The best evidence for a hexavalent Po is a recent solvent extraction experiment. After Po was extracted from HNO_3, HCl or H_2SO_4 solution into methylisobutylketone, the addition of a strong oxidant (Ce^{+4}, Cr^{+6}) displaced the equilibrium in favor of the aqueous phase. Reduction of the oxidant reestablished the initial distribution in the case of Ce^{+4} and led to an intermediate distribution with the bichromate, probably due to incomplete reduction. An approximate value of 1.5 volts was assigned to the Po^{+4}/Po^{+6} couple.[13]

Electrode Potentials Table II gives representative values of Po electrode potentials.

TABLE II

ELECTRODE POTENTIALS OF POLONIUM

Po^{0}/Po^{+2}	Po^{+2}/Po^{+4}	Po^{0}/Po^{+4}	Reference
+ 0.6 volt	+ 1.1 volt	+ 0.8 volt	14
+ 0.38 volt[a]	+ 0.72 volt[a]	+ 0.55 volt[a]	15

a) Measurement made in HCl and refers to complex ions.

From the observed values of the electrode potential Po^{o}/Po^{+4}, it appears that Po lies between Te and Ag in the electrochemical series, in agreement with its behavior in solution towards reducing agents.

<u>Reducing Agents</u> Stannous Chloride-Metallic polonium is immediately precipitated from solution by the addition of $SnCl_2$.[16]

Sulphur Dioxide-Trace Po is precipitated from dilute HCl[17] or HF[18] solution, together with Se and Te, by the action of SO_2 or sulfite, but does not precipitate with Te when the reduction is carried out in concentrated HCl.[19]

Hydrazine--In concentrated HCl, hydrazine reduces Po only to the bivalent state[9,20] but Te and Se are reduced to the metal. Hydrazine reduction in moderately concentrated HCl solution has been used to separate trace Po from Te[21] and from Au, Hg, Pt, and Te[22]. The precipitation of trace Po with Se from HF solution by reduction with hydrazine[23] may be due to adsorption of the Po on the Se precipitate or to the formation of a polonium selenide.

For a more comprehensive discussion of reducing agents see reference 5, p. 28.

4. Soluble Salts

<u>Polonium Fluoride</u> Although no fluoride salts of Po have been isolated, Po is quite soluble in HF. Solutions containing 2

curies of Po per ml of 1 N HF are reported to be unsaturated.[24] Attempts to prepare a volatile fluoride by reaction with F_2 gas,[6] or with liquid BF_3[25] have been unsuccessful. However recent work with 1 mg of Po^{208} indicated the formation of a volatile Po compound, which decomposed before it could be isolated.[26]

Polonium Tetrachloride The bright yellow salt is hygroscopic and hydrolyzes rapidly. It dissolves in HCl with complex formation, in thionyl chloride and in water with slow hydrolysis. The salt is moderately soluble in ethyl alcohol, acetone, and some other ketones.

Polonium Dichloride The dichloride is a dark ruby-red solid which dissolves in dilute HCl (probably with complex formation) to form a pink solution. It is rapidly oxidized by autooxidation and also by chlorine water or hydrogen peroxide.

Polonium Tetrabromide The tetrabromide is a bright red solid which is soluble in dilute HBr, ethyl alcohol, acetone and some other ketones. It is sparingly soluble in liquid bromine and insoluble in benzene and carbon tetrachloride. The solid is hygroscopic and on hydrolysis yields a white solid.

Polonium Dibromide The dibromide forms a purple solution in 2 N HBr. It is rapidly converted to the quadrivalent state by alpha autooxidation.

Polonium Acetate Solubility of polonium in acetic acid increases from 0.88 c/l (0.195 mg/l) in 0.1-N acid to 375 c/l (83.2 mg/l) in 2 N acid.[27] Complex ion formation is indicated.

Polonium Tartrate $PoCl_4$ is very soluble in 2 N tartaric acid, indicating some type of interaction.

Polonium Disulfate The disulfate is a white solid which is very soluble in dilute HCl. It is insoluble in acetone or ethyl alcohol, and may be hydrolyzed in the latter. The preparation of the salt utilizes its insolubility in 0.5-5.0 N H_2SO_4.

Basic Polonium Sulfate A compound of probable composition $2PoO_2-SO_3$ is more soluble in dilute H_2SO_4 than the disulfate, and it also is readily soluble in dilute HCl.

Basic Polonium Selenate Analogous to the basic sulfate, a compound of probable composition $2PoO_2-SeO_3$ is insoluble in 0.015-5 N selenic acid, but it is very soluble in dilute HCl.

Bivalent Polonium Sulfate The compound is soluble in 1-2 N H_2SO_4 and forms a pink solution characteristic of the bivalent Po ion. Quadrivalent polonium sulfate precipitates after some minutes due to autooxidation.

Polonium Cyanide -- The solubility of Po in KCN increases from 0.39 c/l (0.087 mg/l) in 0.05 M solution to 5.4 c/l (1.20 mg/l) in 1.5 M solution.[27] Complex ion formation is probable.

The solubility of Po in a number of reagents is given in Table III.

TABLE III

SOLUBILITY OF OXIDIZED POLONIUM[a]

Reagent	Conc. (M)	Solubility of Po mc/ml	Solubility of Po mg/l
$NaNO_3$	1.5	1.4	0.31
Na_2CO_3	0.5	1.4	0.31
	0.05	1.6	0.36
$(NH_4)_2CO_3$	0.75	24.0	5.34
	0.25	0.4	0.09
NH_4OH	18	1.0	0.22
H_2SO_4	0.05	2.3	0.51
H_3PO_4	0.5	30.0	6.67
KH_2PO_4	1.0	4.0	0.89
$(NH_4)_2HPO_4$	1.0	1.7	0.38
Na_2HPO_4	1.0	4.8	1.1
Acetic acid	1.0	128	28.5
Sodium acetate	1.0	0	0
Oxalic acid	0.5	42	9.3
KHC_2O_4	0.4	62	13.8
Citric acid	1.0	46	10.2
KCN	1.0	3.8	0.84
$KHC_4H_4O_6$	1.0	41	9.1

a) Taken from Reference 6, p.53.

5. Insoluble Compounds of Polonium and Coprecipitation Behavior

Polonium Hydroxide (Probable composition $PoO(OH)_2$) On the milligram scale, a pale yellow flocculent precipitate is obtained by the addition of aqueous ammonia or alkali hydroxide to acid solutions of freshly prepared $PoCl_4$ or $PoBr_4$. A study of the solubility of the hydroxide in KOH indicates that some Po may be lost as a polonite at higher hydroxide concentrations.[27] For the probable reaction

$$PoO(OH)_2 + 2\ KOH = K_2PoO_3 + 2\ H_2O,$$

$$K_c = \frac{K_2PoO_3}{KOH} = 8.2 \pm 0.4 \times 10^{-5}.$$

Because of this, ammonia is the preferred precipitating agent under normal circumstances. The solubility of the hydroxide in 18 $\underline{M}$ NH_4OH has been variously reported as 0.20 mc/ml (0.044 mg/l)[27] and 1.0 mc/ml (0.22 mg/l).[6] The solubility in 0.1 $\underline{N}$ NH_4OH was determined to be 3.7×10^{-5} mole/l (7.8 mg/l) and the solubility product of $Po(OH)_4$ calculated to be 10^{-37}.[28] The hydroxide is readily soluble in most acids.

Trace Po is carried almost quantitatively by $Bi(OH)_3$ in ammonical solution, probably by an adsorption process. The hydroxides of Fe^{+3}, La, and Al have also been used as carriers for Po in alkaline solution. Colloidal Pt and coagulated AgOH or $Fe(OH)_3$ sols have been used to carry Po.

Polonium Monosulfide The monosulfide is formed as a black precipitate by the action of H_2S on $PoCl_2$ or $PoCl_4$ solutions in dilute HCl. The formula has been established from experiments on the milligram scale.[10] The solubility product is about 5×10^{-29};[10] however, trace amounts can be dissolved in concentrated HCl. Milligram amounts are comparatively soluble in conc. HCl but also dissolve slowly in dilute HCl, probably due to Cl_2 from alpha bombardment of the solvent. The monosulfide is readily decomposed by Br_2, aqua regia and sodium hypochlorite solutions, or by heating under vacuum. Polonium disulfide is unknown.

Trace Po can be precipitated by H_2S from acid solution along with other insoluble sulfides. Since PoS is less soluble in acid than BiS, trace amounts of Po can be separated from massive amounts of BiS[29] (or TeS[30]) by leaching with 1 N HCl.

Polonium Formate A black precipitate of uncertain composition and low solubility is formed by treating polonium hydroxide with 2 N formic acid.

Polonium Tetraiodide The tetraiodide can be formed by treating polonium hydroxide or dioxide with 0.1 N HI. It is precipitated from dilute HCl solutions of Po by the addition of 0.1 N HI. The tetraiodide is a volatile black solid which is slightly soluble in ethyl alcohol (1 g/l) and in acetone, and is slowly hydrolyzed to a white solid in water. It is insoluble in 2 N HCl, 1-2 N HNO_3, acetic acid, chloroform, benzene, CCl_4 and diethyl and dibutyl ethers. It is decomposed by hot conc. HNO_3 or sodium hypochlorite and slowly by conc. KOH solutions. It is somewhat soluble in 2 N HI indicating complex formation.

Coprecipitation with Tellurium Metal and Compounds A finely divided precipitate of Te metal formed by reduction in situ with $SnCl_2$ carries Po and affords a separation from massive amounts of Bi. The Te can be eliminated by dissolving the precipitate in conc. HNO_3, adding conc. HCl and precipitating the Te with SO_2.[31] Under these conditions the Te does not carry Po. The effect of acid concentration on the coprecipitation of Po^{206} tracer with Te metal has recently been investigated.[32] (See Procedure XV.) Reduction with $SnCl_2$ in HCl produced a precipitate which carried the Po nearly quantitatively up to an acid concentration of about 6 N. With SO_2 reduction, the non-carrying is essentially quantitative at 2 N HCl or higher, but at the lowest acid concentration (0.3 N) the carrying was nearly quantitative. Hydrazine has also been used to reduce Te without coprecipitation of Po.[21]

Polonium can be separated from Bi in very dilute HNO_3 solution by precipitation with $PbTeO_4$. The Pb is subsequently removed as the sulfate, and the Te is precipitated with SO_2 leaving a comparatively pure solution of Po.[19] (See Procedure XX for more details.)

Coprecipitation with Selenium In the presence of Se, Po is precipitated almost quantitatively by hydrazine or SO_2 from solution in HCl[17] or HF.[23] The carrying may be due to the formation of polonium selenide.

Other Precipitation of antimony or bismuth pyrogallate from 0.05 N HNO_3 solution[33,34] or thioglycollic β aminonaphthalide (thionalide) from neutral solution[35] will carry Po but will also carry RaE (Bi^{210}).

Hydrolysis and Radiocolloidal Behavior of Polonium Centrifugation experiments have shown that Po is not hydrolyzed in 1 N HCl but considerable hydrolysis does occur in 0.01 N HCl[36,30]. In HNO_3 a maximum precipitation of Po was observed at $2\text{-}4.7 \times 10^{-5}$ N.[37] However, when the walls of the container were coated with paraffin wax, very little Po could be centrifuged from 6×10^{-4} N HNO_3[38] which suggests that the precipitation is affected by the traces of silica dissolved from the walls of the vessel.

Trace Po is very readily adsorbed from dilute acid solution onto glass, and it is extremely difficult to remove the adsorbed Po by acid washing. The adsorption is reported to be most marked from solutions in 0.1 N acid and is a minimum close to the neutral point.[39]

In neutral, weakly acid or alkaline solutions Po appears to form a colloid. Since there is some doubt that true colloids are involved, the term "radiocolloidal" has been used to describe this behavior. The radiocolloidal behavior of Po at trace concentrations is adequately covered elsewhere.[40, 41, 42]

From a practical standpoint, Po containing solutions should be maintained in acid solutions of at least 1 N whenever possible. In other cases coating the glass vessels with paraffin wax, or the use of polyethylene may prevent "losses" of Po. Impurities have a marked influence on radiocolloidal formation, so that careful purification of reagents may diminish or prevent radiocolloidal formation.

6. Complex Ions

Hexachloride A study of the absorption spectra of HCl solutions of Po by Hunt[43] at Mound Laboratory has indicated that at least two complexes are formed. Evidence indicated that the formulas of the complexes were $Po(OH)Cl_b$ and $PoCl_{b+2}$ with the latter present in HCl concentrations above 1 N. (The value of b was not determined.) The equilibrium constant for the reaction

$$Po^{+4} + 6\ Cl^{-} = PoCl_6^{-2}$$

has been estimated from electrochemical data to be of the order of 10^{14}.[15] Recent work with Po on the milligram scale has resulted in the isolation and characterization of a number of hexachloropolonite salts. If $CsCl_2$ is added to a solution of $PoCl_4$ in HCl, a yellow precipitate of $CsPoCl_6$ is formed immediately. The Rb^+, K^+, NH_4^+ or tetramethylammonium salts are soluble in HCl, but can be prepared by evaporation of an HCl solution of $PoCl_4$ with the corresponding univalent chloride.[44, 9] The ammonium salt can also be prepared by heating the solid tetrachloride with NH_4Cl.[9] All of the salts are yellow and have a face-centered cubic structure. They are isomorphous with the corresponding Te and other similar quadrivalent metal complex salts.

Hexabromides Dissolution of $PoBr_4$ in dilute HBr probably forms the ion $PoBr_6^{-2}$ since addition of $CsBr_2$ produces an immediate red precipitate of $CsPoBr_6$. The ammonium salt can be formed by heating $PoBr_2$ in NH_3 gas at 100°C. The salts are isomorphous with the corresponding hexachloropolonite and hexabromotellurite salts.

Hexaiodides Polonium tetraiodide is the least soluble of the tetrahalides, but a study of its solubility in HI indicates formation of a hexaiodopolonite. The equilibrium constant for the reaction

$$PoI_4 + 2I^- = PoI_6^{-2}$$

was determined to be 5.9×10^{-3} at 22°C.[45] At low HI concentrations, a pentaiodopolonite may be formed. Black $CsPoI_6$ is obtained by the addition of a Cs salt to a solution of Po in 2 N HI. It is isomorphous with $CsTeI_6$.

Polonium Acetylacetonate Pale yellow needles were obtained by evaporating an acetylacetone extract of Po and recrystallizing from petroleum ether. When $PoBr_2$ or $PoCl_2$ reacted with acetylacetone, two molecules of halogen acid gas were evolved for each molecule of starting material. The resulting highly colored materials (Cl-yellow, Br-orange) were soluble in excess ketone. They readily lost the remaining halogen on warming or shaking with aqueous KOH, giving a volatile purple solid. After a few days, alpha radiation destroyed the complex, or the complex could be decomposed immediately by hot fuming HNO_3. A cyclic structure formed by condensation of the Po halide across the terminal methyl groups of the diketone was suggested, analogous to a known tellurium compound.[20]

Polonium-EDTA complex (EDTA = ethylenediaminetetraacetic acid) Yellow $PoCl_4$ in 2 N HCl can be titrated with 0.0015 M EDTA to a colorless end point. A 2:1 complex was indicated. However, solubility studies of $PoCl_4$ in 0.001 M EDTA indicate a 1:1 complex.[46] The complex is soluble in both acid and alkaline media, but is more stable in alkali. However, the complexing agent is rapidly destroyed by the oxidizing effect of alpha bombardment, from milligram amounts of Po.

Other Acetic acid, tartaric acid and cyanide ion probably form complexes which account for the solubility in those reagents.

7. Solvent Extraction

In the absence of organic complexing agents Since Po forms a number of complex halides in solution, it is natural to expect that some of these compounds could be extracted into organic solvents. K. Kimura and coworkers[47] found that Po could not be extracted from HCl or HBr solutions with diethyl ether or isopropyl ether. However, Po was extracted with isopropyl ether or methyl isobutyl ketone from HCl solutions containing KI. Procedure IV gives the details for the extraction with isopropyl ether.

The extraction of Po from various acids with diisopropyl ketone has been studied.[48] In HCl, the highest extraction reported was

97 per cent from 3 N HCl in the presence of 0.5 M KI. Extraction from HNO_3 or HNO_3/HCl mixtures was less efficient, and no extraction was observed from HF. Other ions found to be extracted from 6 N HCl were Tl^{+3}, Pa^{+5}, Tl^{+1}, Fe^{+3} and small amounts of uranyl ion. No appreciable amounts of RaD or RaE were extracted. Total extraction was observed from 12 N H_2SO_4 and yielded a radiochemically pure solution.

Diisopropyl carbinol and diisobutyl carbinol have also been used to extract Po from HCl solutions.[49]

Tributyl Phosphate (TBP) A partition coefficient of 110 in favor of the organic phase has been reported for the extraction of Po from 6 N HCl by a 20 per cent solution of TBP in dibutyl ether.[50] Any Bi extracted into the organic phase can be removed by washing with 6 N HCl. The Po can be recovered by stripping the organic with conc. HNO_3. This method is illustrated in Procedure VI. Polonium is also extracted by TBP from a H_2SO_4-$FeSO_4$ solution (see Procedure VIII).

The extraction of millicurie amounts of Po into 10 per cent TBP/dekalin as a function of HCl concentration has been investigated.[51] The partition coefficient reaches a maximum (ca. 60) between 7 and 9 M HCl. The extraction is quite small at low HCl concentrations so it should be possible to strip Po from the organic phase with 0.5-1 N acid. The equilibrium constant for the reaction

$$PoCl_4 + 2\ TBP = PoCl_4\text{-}2TBP$$

is reported to be 0.04 at room temperature.[51]

Thenoyltrifluoroacetone (TTA) Polonium is extracted from HCl solutions (pH 1.3 and up) by solutions of 0.25 M TTA in benzene.[52] Thorium and Bi will also be extracted to some extent, but with the proper control of pH, separations from Pb, Ac, and Tl could be achieved. Procedure XIII gives the details of the method.

Dithizone Chloroform solutions of dithizone have been used to extract trace Po from acid solutions of radiolead[53, 54, 55] and about 95 per cent of the Po is extracted from HNO_3 or HCl solutions between pH 0.2 and pH 5.[53] The extraction of "weighable" amounts of Po at low acidities (pH greater than 2) is extremely irreproducible and this is apparently due to the hydrolysis of the Po compound present in the solution. Trace Po can apparently be stripped from the organic phase with 4 N HCl. Dithizone can also be used to extract trace Po from ammoniacal KCN or ammonium citrate solutions[55] and it has been used to separate radiochemically pure RaE from radiolead.[56]

Polonium Diethyldithiocarbamate Trace Po can be extracted with chloroform, carbon tetrachloride or amyl alcohol from ammonium acetate-acetic acid buffered solutions (pH 1.0--6.8) containing sodium diethyldithiocarbamate. At pH 1 (without ammonium acetate buffer) 93 per cent of the Po was extracted into $CHCl_3$. Evidence indicated a 1:1 compound was formed.[47]

Polonium Hydroxyquinolate Extraction of trace Po from aqueous solution with a $CHCl_3$ solution of 8-hydroxyquinoline has been investigated.[47] In an ammonium acetate--acetic acid solution buffered at pH 3.4, 74 per cent extraction was observed. A 1:1 Po complex is probably formed.

Tri-n-benzylamine Extraction of over 99 per cent Po from 6 N HCl with a 5 per cent solution of tri-n-benzylamine in chloroform has been reported.[57] The extraction probably depends upon the formation of a water insoluble amine-$PoCl_x$ compound. Other metals which form complex anions (e.g. Pu, Zr, and Pa) are also extracted by this reagent from various acid media.

8. Ion Exchange and Paper Chromatography

Cation Exchange Polonium can be separated from Bi (RaE) by adsorption on Dowex*-50 (50-100 mesh) resin from 0.1-0.3 N HCl solutions, followed by elution of the Bi by 2 N HNO_3 and of the Po by 2 N HCl.[58] This work has recently been confirmed.[32] The separation can also be carried out on Amberlite** IR-1 (40-60 mesh) resin, from which the Bi can be eluted with 3 N HNO_3.[59] The adsorption of Po by Amberlite IR-120 from 0.05-2.5 N HCl and 0.1-5.0 N HNO_3 has been investigated.[60] In each experiment the initial concentration of Po was approximately 2×10^{-10} M. The adsorption was done on a batch basis and each batch was given time to come to equilibrium before sampling and counting. In HCl the distribution coefficients (Po per mg of dry resin/Po per ml of solution) ranged from 150 at 0.05 N to less than 1 at concentrations above 0.2 N. The distribution coefficients were higher in HNO_3, being over 10^3 at the lowest acid concen-

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* Trade name of Dow Chemical Co., Midland, Michigan

** Trade name of Rohm & Haas Chemical Co., Philadelphia, Pa.

trations. Even in 5 N HNO_3 the coefficient was around 4. It was also observed that the addition of oxalic acid to HNO_3 solutions of Po greatly reduced the coefficient.

Procedure XVIII describes the behavior of Po, Te and Bi on Dowex-50.

Anion Exchange Polonium is strongly absorbed from 0.05-12 N HCl by the strong base resins such as Dowex -1, -2, and Amberlite IRA-410.[60] The value of the distribution coefficient ranges from approximately 1.5×10^5 in low acid concentrations to 2×10^4 at the high acid concentrations. The adsorption from HNO_3 media is much less (123 at 0.8 N, 90 at 5 N) and it takes much longer to reach equilibrium (in some cases a week).[60] A separation of Po from the other Group 6B elements has been made on Dowex-1 X 4 resin.[61] Trace Po, Se and Te are absorbed from 12 N HCl. Selenium is eluted by 6 N HCl, Te by 2 N HCl and Po by 1 N HNO_3. However, recent work[32] has failed to confirm that Po is eluted by dilute HNO_3.

Ishimori used Amberlite XE-98 to separate carrier-free Po from a RaDEF mixture. Solutions of 2 N HCl, 12 N HCl and 7 N HNO_3 were used as elutriants for RaD, E, F, respectively.[47]

Procedure XIX describes the behavior of Po and Bi on Dowex A-1 resin.

Paper Chromatography Recently the techniques of paper chromatography have been applied to separations of Po. A mixture of 50 parts butanol, 15 parts pyridine, 5 parts concentrated hydrochloric acid, 10 parts acetic acid and 10 parts water produced a good separation of a RaDEF mixture.[62] Mixtures of Bi, Po, Te and Se were separated using a developing solution consiting of 60 g of 49 per cent HF per 100 ml of methyl ethyl ketone.[63] A number of combinations of ketones or ethers and alcohols were found to separate Bi and Se but the separation of Po and Te was poor.

The developed paper strips can be read by autoradiographs, or by passing the strip slowly past a detector with a narrow slit window.

A separation of Po and Pb using n-butyl phosphate and acetone is given in Procedure IX.

9. Sublimation Techniques

Early in the work on Po, it was found that mixtures of Po and Bi sulfides could be separated by vacuum sublimation. This method has been used for the rapid purification of high-level Po residues containing appreciable amount of decay lead.[10] (See procedure XII)

In general, sublimation techniques have been used to build up relatively concentrated (millicurie) sources from a number of smaller electrodeposited sources. Work on the trace level has produced somewhat erratic results, but this may be due to incomplete degassing of the support metal, or possibly diffusion of the Po into the support metal.

In air, Po begins to sublime at 700°C and is completely vaporized at 900°C, while scarcely any Bi (RaE) sublimes below 1100°C.[64, 65] The product of sublimation in air is probably the dioxide, but in vacuum the product has been shown to be the metal.[9] Nitrogen and hydrogen have been used as carrier gases during the distillation of Po, but require a temperature of 900-1000°C. Vacuum distillation takes place at 500°C.

Foils of Cu, Ni, Au, Pt and Pd, and Pd wires have been used to condense the Po. Platinum and Pd condense the Po preferentially over Cu or Ni, but no satisfactory explanation has been given. The use of Cu foils is usually unsatisfactory because the product is contaminated with CuCl. At the higher temperatures necessary for the sublimation in H_2 or N_2, Au fuses and encloses the Po. Gold is therefore satisfactory only for vacuum sublimation.

Since Po is more volatile than either Pb or Bi, distillation procedures have been investigated.[6] Polonium is effectively separated from irradiated Bi, but a major problem is finding a material which will withstand the corrosion of molten Bi.

A number of organic Po compounds show remarkable volatility.[47] Compounds of Po with diphenylcarbazone and diphenylcarbazide exhibit volatility below 100°C/1 atm., and the compound with diphenylthiocarbazone (dithizone) is volatile at 115°C. In the latter case, the distillate was collected on a Pt dish a few cm above the sample and identified as Po dithizonate. A mixture of RaD, E, F has been separated by distillation in the presence of diphenylcarbazide. The details are given in Procedure V.

10. Spontaneous Deposition and Electrodeposition

One of the characteristics of Po is its ease of deposition; either by chemical deposition on less noble metals or by electrodeposition. This ease of deposition coupled with its characteristic volatility has probably hindered the development of procedures based on newer methods, such as solvent extraction or ion exchange. Most of the commonly used separation procedures involve a deposition step either as a final step (e.g. plating on a metal disk for counting) or as a means of concentrating Po from relatively dilute solutions. Although spontaneous deposition is simpler than electrodeposition, spontaneous deposition has the disadvantage that the electrode potential is fixed by the selection of the metal. Since the deposition potential for Bi is close to that of Po, in many cases Bi(RaE) is also deposited. Electrodeposition permits a control of potential, and separation from Bi can be assured. Electrodeposition can be used to plate larger quantities more efficiently and has the further advantage that no metal ions are added to the solution. Thus electrodeposition is generally used for plating high level solutions or where purity is a primary concern. A number of metals and the conditions used for deposition are discussed below.

Spontaneous Deposition on Silver

Marckwald[17] found that Po deposited readily on Ag from dilute HNO_3 or HCl solution; during the deposition a black film appears on the Ag and this may consist of either an oxide or peroxide.

The deposition is improved, and the Ag foils are much cleaner if the solution is boiled with SO_2 prior to the deposition[66] or if hydrazine is present in the solution during the deposition.[22]

Polonium also deposits on Ag from acetic acid solutions and the deposition is improved in the presence of small amounts of HCl.[67, 68]

The deposition of Po from HCl solutions proceeds more smoothly and is more efficient than that from HNO_3, H_2SO_4 or acetic acid solutions, although the deposition from HNO_3 is reported to give less surface oxidation of the Ag foil.[67] Most of the Po can be recovered from HCl solutions by scavenging with a succession of fresh foils and overall recoveries of 90 per cent are commonplace. The deposition is inhibited by Au, Hg, Pt, or Te and these impurities must first be removed by reduction with hydrazine in 20 per cent HCl or acetic acid solution.[22] Small amounts of ferric ion also inhibit the deposition, but this can be overcome by reduction with ascorbic acid or SO_2, or by complexing with fluoride ion. The deposition proceeds more smoothly at higher temperatures and at 97°C over 99 per cent of the Po is deposited from 0.5 N HCl (see Procedure II). Milligram amounts of Po are readily deposited on Ag wool, powder or foil from dilute HCl.[69] The most efficient depositions are achieved by depositing from hot solution in the presence of reducing agents (hydrazine or SO_2) and HCN; the latter dissolves the AgCl formed in the electrochemical replacement.[70]

Trace Po also deposits on Ag from 0.1 N KOH or NaOH but not from ammonical solution. The deposit is easily removed by treatment with hot concentrated alkali.[71]

Spontaneous Deposition on Copper

Copper has been used to separate Po from aged Ra solutions and from radiolead solutions. The deposits always contain some RaE.[65] Deposition on Cu has the disadvantage in certain situations that when Po is sublimed from Cu, the product may be contaminated with CuCl.

Spontaneous Deposition on Nickel

Trace or milligram amounts of Po deposit readily on Ni from dilute (0.1-1.0 N) HCl solutions.[72] The deposit may contain RaE and possibly RaD. Deposition from 0.1-0.2 N HNO_3 has been used, but HNO_3 sometimes oxidizes the surface and is generally less satisfactory than HCl.

Spontaneous Deposition on Bismuth

Polonium will deposit slowly on Bi from HCl or H_2SO_4 solution causing the Bi to become bronze colored. One method of separating Po from irradiated Bi makes use of this deposition.[6] The Bi is dissolved in HCl-HNO_3 mixture and the excess nitrate ion removed by one of the methods given in Sect. IV (p.41). A small amount of Bi metal is added and the Po deposits on it. The cycle can be repeated until the desired concentration is achieved.

Deposition on Noble Metals

In the presence of reducing agents, Po deposits on Pt or Pd from dilute HCl solutions. Hydrogen gas has been used as a reducing agent,[73, 74] and has the advantage over electrochemical replacement that no metal ions are added to the solution. RaE is also deposited. In the presence of thiourea, Po deposits on Au from 1 N HCl and affords a good separation from RaE.[73, 74] Due to the stability of the gold-thiourea complex Au has an oxidation potential of about +0.20 volt which lies between the values of the potential of Bi and Po at the concentrations used. Consequently, only the Po deposits on the Au.

Electrodeposition of Polonium

Trace Po in solution in acetic acid can be cathodically deposited on Pt at a current density of 4 μamp/cm^2; Bi is deposited at higher current densities (approx. 10 μamp/cm^2).[75] Polonium can also be deposited from solution in trichloroacetic acid.[76]

Reports of the cathodic deposition of trace Po from HNO_3 are rather conflicting. The deposition is said to take place under conditions in which Pb is deposited on the anode[77] and deposition on a Au cathode is preferable.[78] The use of a rotating disc cathode has also been recommended. Current densities of the order of 30 μamp/cm^2 have been quoted in the literature[79,80] and although the procedure separates Po from Pb, the product still contains a good deal of Bi. I. Curie,[67] however, found that the cathodic deposition of Po from HNO_3 was generally unsatisfactory, because part of the Po deposited on the cathode, a mixture of RaD and Po deposited on the anode and a variable amount of Po remained in the solution from which it could not be removed by electrolysis; quantitative yields were only obtained when the Po was plated on the anode. Other workers (e.g. [64, 81]) have reported reasonably efficient cathodic deposition yields and current densities of the order of 10-20 μamp/cm^2 were used (e.g.[82, 83, 84]). It is probably better to deposit trace Po anodically in the presence of impurities such as dust or silicic acid, although the Pb will also be deposited from solutions containing high concentrations of HNO_3. The anodic deposition separates Po from adventitious Hg, Au, or Pt [85, 80].

Large amounts of Po can be electroplated from a variety of acid media, but HNO_3 is probably the most satisfactory. High concentrations of pure Po are normally plated at 0.0 volt with respect to the normal calomel electrode from 1.5 N HNO_3.[6] Platinum anodes and Pt gauze cathodes are preferred. Gold may be used for the cathode, but not for the anode since it would dissolve and be plated on the cathode along with the Po. Tantalum, Mo, and C electrodes have also been used. Electrodeposition from HCl solutions require special precautions. Platinum anodes dissolve in this medium and the Pt is plated on the cathode. Graphite anodes are satisfactory provided they have been bonded to prevent flaking and have been treated to prevent the adsorption of Po.[6]

Plating from H_2SO_4, H_3PO_4 and $HClO_4$ is hindered by the low solubility of Po in those media, but plating from 1 N HF reportedly gives excellent deposits. A number of organic acids have been tried as plating media. In general the plating times are long and the deposits are rather porous.[6]

IV DISSOLUTION OF SAMPLES

As the section on soluble compounds indicated, Po is soluble in most mineral acids, so that trace Po will be dissolved by any reagent which dissolves the gross matrix. A few of the more common cases are discussed below:

In the case of Po in irradiated Bi, the Bi may be dissolved in a mixture of HCl and HNO_3 acids (ratio between 1:4 and 3:4). Hydrochloric acid alone will not dissolve the bismuth easily. However, the HNO_3 will often interfere at a later step and must be removed. If the sample volume is not too large, the HNO_3 can be removed by repeatedly adding conc. HCl and evaporating to a small volume. Alternatively, formic acid or formaldehyde will reduce the HNO_3. Urea has been used for this purpose, but it removes only the nitrous acid. However, Bi dissolves only slowly in the absence of nitrous acid so that Bi metal can be readily used as a deposition medium. For a more detailed analysis of the problems of dissolving and processing large amounts of irradiated Bi see reference 6. Procedure VI describes the dissolution of Bi targets and Procedure V describes the dissolution of Pb targets.

In the case of biological studies, it is often necessary to analyze for Po in large amounts of tissue or other organic material. The usual procedure uses a wet oxidation in $HClO_4$-HNO_3 medium to destroy the organic material. (Caution: The use of $HClO_4$ in the presence of organic matter presents a potential explosion hazard.)

Procedure III gives one method of preparing samples from biological sources.

V. COUNTING TECHNIQUES

The counting of Po isotopes presents special problems. All of the naturally occurring Po isotopes decay by alpha emission with energies above 5 Mev. Gamma radiation is associated with a few of the isotopes, but consideration of the alpha-gamma branching ratio and the half-life excludes gamma counting in most cases. However, gamma counting of trace Po^{206} has been used in one instance (See Note to Procedures XIV-XIX p. 66).

A reasonable amount of care should be exercised in the preparation of alpha counting mounts to prevent volatilization of the Po. Since the halides are considerably more volatile than the nitrate or oxide, it is preferable to evaporate HNO_3 solutions. The mounts should not be flamed nor subjected to excessive heat.

VI COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR POLONIUM

Procedure I

THE DETERMINATION OF POLONIUM-210 IN URINE

Source: LA-1858 (2nd edition), p. 172

Procedure

1. The urine sample is collected in a 1/2 pint waxed paper container and stored in a refrigerator (3°C) if the time between collection and analysis is greater than one hour.

2. Measure 100 ml of the urine sample with a graduate and pour into a 150 ml beaker. Rinse the graduate with 20 ml of 6 N HCl and add to the urine. Place the sample in a constant temperature bath at 50-55°C.

3. Degrease a Ni disc in CP trichloroethylene, dip in conc. HNO_3, rinse in H_2O, dip in conc. HCl, and rinse in H_2O. Make sure the surfaces are bright.

The Ni discs are made from 0.025 in. "commercial pure" Ni sheet. The discs have a 7/8 in. diameter, with a 1/8 in. hole set 1/16 in. from the edge.

4. Suspend the disc on glass stirring hook in the urine and stir the solution mechanically for one hour.

The stirrers are glass rods bent into a hook to hold the plate in the solution. A Model I electrically driven stirrer, manufactured by Eastern Industries, New Haven, Conn., is used at LASL.

5. Remove the disc from the urine and rinse down the glass

stirring hook and disc with a fine stream of distilled water. Let the plate hang in air until dry.

6. Count the alpha activity with a low-background proportional counter on each side of the disc for 30 minutes. Add the two counts, subtract the counter background and report the activity of the sample as d/m/liter of urine.

Calculation

$$\frac{\text{total c/m - counter background}}{\text{counter efficiency}} \times \frac{1000\text{ ml}}{\text{ml of sample}} = \text{d/m/liter}$$

Procedure II

PRECISION PLATING OF POLONIUM

Source: I. Feldman and M. Frisch, Anal. Chem. 28, 2024 (1956) Dec.

Procedure

The apparatus used was similar to that of Eutsler, Milligan and Robbins (USAEC Rept. LA-1904), in that a metal foil disk (0.003 in. thick and 1.5 inches in diameter; Ag in our case) was suspended in the Po solution by a glass stirring rod hooked through a 1-mm hole in the foil. The Po solution was contained in a 300-ml tall-form beaker without a lip, which was suspended in a water bath through a sheet of copper containing six holes, each large enough to pass all but the rim of the beaker. Thus, six solutions could be plated simultaneously. The idea first suggested by Baxter and Wood (USAEC Rept UR-269) of operating all the stirrers with one motor by means of a pulley and belt system was adopted. After plating, both sides of each Ag foil were counted in scintillation counters.

In a series of experiments one ml of stock Po^{210} solution (containing about 3000 cpm) was diluted with 200 ml of 0.5 N HCl. When the bath reached 97°C, plating was started. The first disk was exposed for 1.5 hours. Then a second disk was exposed for 2 hours. Finally, a third disk was exposed for 2 hours. The sides of the beakers were washed down with distilled water after each hour of plating time.

Plating efficiencies ran as high as 99.8 ± 0.2 per cent for the average of three solutions, for one plating. This is well within the probable counting error of 0.5 per cent. These results have been reproduced repeatedly. Experiments also showed that failure to wash down the sides of the beaker during the experiment introduces an error of about 1 per cent. A negligible amount of polonium was found to be adsorbed on the glass. Third platings always showed background only.

Procedure III

WET OXIDATION OF BIOLOGICAL SAMPLES

Source: W. L. Minto, National Nuclear Energy Series, Div. VI,
Vol. 3, pp. 15-18.

1. With the sample in a Kjeldahl flask (wt in g of sample not over 5 per cent of volume of flask) add 3 ml $HClO_4$ and 1 ml HNO_3 per gram of sample.

2. Immerse the flask in a boiling-water bath until the foaming subsides (5 to 20 minutes depending on sample size)

3. Add 1 or 2 glass beads to prevent bumping and transfer the flask to an air bath prepared as follows: Place a 6 in. square of asbestos paper, with a 1 in. diameter round hole cut through its center, upon a 6 in. asbestos centered wire gauze. Support the gauze by a ring over a Meker burner, and clamp the flask in position over the hole in the asbestos paper with its bottom just clearing the gauze.

4. Heat the sample until the solution becomes water white (pale yellow if much iron is present) and copious white fumes of $HClO_4$ are emitted.

4a. If the sample is large or contains much fat, the solution will turn brown and foam slightly. Remove the burner and allow the reaction to subside. Add a few drops of concentrated nitric acid, allowing it to run down the inside of the flask. (Excessive foaming results if the HNO_3 is dropped directly into the solution.) Resume heating until $HClO_4$ fumes are given off or the solution turns brown again. In the latter case repeat step 4a.

5. To prepare the solution for the deposition of Po, add a few ml of water and a few drops of indicator*. Neutralize most of the $HClO_4$ with pellets of NaOH, and continue by the dropwise addition of a strong NaOH solution. Immediately after neutralization add conc. HCl in such volume that when the sample is made up with water to a volume suitable for aliquoting, the resulting solution will be 0.5 N in HCl.

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* The recommended indicator is made by dissolving 50 mg of methyl red and 125 mg bromthymol blue in a mixture of 85 ml 95 per cent alcohol and 15 ml water. This indicator is red below pH 4, orange at pH 5, yellow at pH 6, green at pH 7, and blue at pH 8 and above.

Procedure IV

SOLVENT EXTRACTION SEPARATION OF POLONIUM

Source: K. Kimura and T. Ishimori, "Some Studies on the Tracer Chemistry of Polonium", Proc. Second U. N. Internatl. Conf. on Peaceful Uses of Atomic Energy, Geneva, 28, 151, P/1322, 1958.

An aqueous solution of Pb^{210} and its daughters (RaDEF mixture) is made 0.25 M in KI and 3 N in HCl respectively. One ml. of the solution is transferred to a separatory funnel containing 4 ml of isopropyl ether. Polonium is extracted into the organic phase with gentle swirling, while Pb and Bi (RaD and -E) remain in the aqueous phase and are discarded. Polonium is then scrubbed from the organic phase by shaking with 1 ml of 3 N HCl. The resulting HCl solution is free from Pb^{210} and Bi^{210}, and contains Po^{210} alone. A yield of approximately 80 per cent is obtained for the separation of Po and the time required for the extraction is less than 20 min.

Procedure V

DISTILLATION SEPARATION OF POLONIUM

Source: K. Kimura and T. Isimori, "Some Studies on the Tracer Chemistry of Polonium", Proc. Second U. N. International Conf. on Peaceful Uses of Atomic Energy, Geneva, P/1322, 28, 154, 1958.

Hisao Mabuchi, Nippon Kagaku Zasshi 80, 714-8 (1959); Chemical Abstracts 54, 2858g

Fifty milliliters of nitric acid solution of RaDEF mixture is taken in an all-glass distilling apparatus. The acidity of the solution should be adjusted between 0.1 and 0.5 N in HNO_3. After the addition of 30 mg of diphenylcarbazide, one-half of the initial volume of the solution is distilled off. Wash the condenser with 2 N HNO_3.

The residue from distillation was adjusted to 0.1 N in HNO_3 and subjected to dithizone-CCl_4 extraction. Fifty-six per cent of RaF was found in the distillate, 37 per cent in the washings and about 7 per cent in the CCl_4 extract. Neither RaD nor RaE was found in the distillate. Ninety-seven per cent of RaD was found in the aqueous phase of dithizone extraction, and approximately 100 per cent of RaE was found in the CCl_4 phase.

Procedure VI

CHEMICAL PROCEDURES USED IN BOMBARDMENT WORK AT BERKELEY

Source: W. W. Meinke, AECD-2738, Sec. 84-1, 1949

Element separated: Polonium	Procedure by: Karraker
Target material: Lead	Time for sep'n: 1 1/2-2 hrs.
Type of bbdt: 380 Mev He^{++}	Equipment required: SO_2 tank

Yield: 80 - 90 per cent

Degree of purification: Very good - less than 1 per cent impurity.

Advantages: Po is separated in a carrier-free state.

Procedure:

1. Dissolve target in 6 N HNO_3.

2. Heat over a burner until the solution is evaporated to conc. HNO_3 (fuming). $Pb(NO_3)_2$ ppts and may be centrifuged off.

Extract twice with equal volume amyl acetate. This removes Tl, Hg, and Au.

3. Add 1 - 2 mg Bi and Tl holdback, then fume with HCl (over a burner) til HNO_3 is destroyed. It will be necessary to take the solution down to a very small volume, add about 8 or so portions of conc. HCl to accomplish this. Dilute the solution by adding 2 volumes of H_2O.

4. Add approximately 1 mg Te carrier. Ppt Te with a few drops of conc. $SnCl_2$ soln. Centrifuge the Te off. This ppt carries Po and At.

5. Dissolve Te in 1 drop conc. HNO_3, then add 0.5 cc conc. HCl.

6. Pass in SO_2 from tank into solution in a hot water bath. Te ppts, carrying At. The solution now is about 6 N in HCl (constant boiling mixture), and contains the Po.

7. Centrifuge off Te. It may be necessary to use Aerosol to coagulate or transfer solution to several test tubes to eliminate Te.

8. Extract the solution with an equal volume of 20 per cent tributylphosphate in dibutyl ether. Po goes into the organic layer. Wash organic layer twice with 6 N HCl to thoroughly decontaminate from Bi.

9. Sample may be prepared by plating a drop of organic solution, or by extracting Po back out with conc. HNO_3. Then dilute the HNO_3, and chemically plate Po on a small piece of clean Ag.

Remarks: Step (3) is very slow and tedious, but can not be avoided, since Pb metal can be dissolved only in HNO_3. It should be noted the Pb is almost untouched in conc. HNO_3, due to the extreme insolubility of $Pb(NO_3)_2$ in fuming HNO_3. About 60 per cent of the Po can be chemically plated on Ag in 10 min.

Procedure VII

CHEMICAL PROCEDURES USED IN BOMBARDMENT WORK AT BERKELEY

Source: W. W. Meinke, AECD-2738, Sec. 84-2, 1949

Element separated: Polonium

Procedure by: Karraker

Target material: Bismuth

Time for sep'n: 40 min. to 1 1/2 hrs.

Type of bbdt: 180 Mev D^+, or 350 Mev H^+

Equipment required: Standard

Yield: 80 - 90 per cent

Degree of purification: less than 1 per cent impurity in sample

Advantages: Po separated in carrier-free state.

Procedure:

Procedure in general is the same as with Pb (see Procedure VI), except for inability to ppt Bi as the nitrate. So step (2) of Procedure VI is eliminated. It is necessary to dissolve Bi metal in HNO_3, but if Bi_2O_3 is used, this can be dissolved in HCl, and necessity for destroying HNO_3 is removed. This shortens the procedure to where it can be done as rapidly as 30 minutes.

Procedure VIII

CHEMICAL PROCEDURES USED IN BOMBARDMENT WORK AT BERKELEY

Source: AECD-2738, Sec. 84-3, 1949

Element separated: Polonium Procedure by: Barton

Milkings from At Time for sep'n: 40 min.

Yield: approx. 90 per cent Equipment required: Test tubes

Degree of purification: At least factor of 10

Advantages: Simplicity.

Procedure:

1. Astatine fraction dissolved in 1-5 ml organic solvent (benzene, carbon tetrachloride, di-isopropyl ether, etc.).

2. Wash with 0.5 ml of 2 N H_2SO_4, 0.25 M $FeSO_4$ solution (to keep At in zero state).

3. Wash H_2SO_4-$FeSO_4$ layer twice with di-isopropyl ether.

4. Extract the Po from the H_2SO_4-$FeSO_4$ layer with 20 per cent TBP in dibutyl ether.

5. Evaporate organic layer on plate with heat lamp. Do not flame or Po will be lost.

Procedure IX

PAPER CHROMATOGRAPHIC SEPARATION OF POLONIUM

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

Elements	Separated From	Decontamination Factor
Po, Bi, Pt, Au, Hg	Pb	10^6

Chemicals	Equipment
n-butyl phosphate, C. P. Acetone, C. P. Eaton-Dikeman Grade 320 Industrial Paper, 0.1 inch or 0.06 inch thick	Glass column with minimum dimensions as follows: diameter-2 inches, height-12 inches.

Procedure

1. The glass column was placed erect in a beaker containing 80 per cent acetone, 20 per cent 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 column was 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 5×10^{-5} gm. per cm. of paper width may be added to the sample.

4. The sample was evaporated to dryness, the residue dissolved in H_2O and the volume adjusted so that a maximum of 1 ml. of solution will be distributed over a minimum of 10 cm. width of paper.

5. The solution was applied evenly across the width of the

paper strip (see Note 1) with a micro-pipet about 3 cm. from the end.

6. The strip was suspended from the glass hook so that the end of the paper was just immersed in the developer. Separations were obtained after the solvent front had travelled 5-6 inches (10-15 minutes).

7. The paper strip was then removed and the various zones identified. The normal R_f values (the ratio of the distance travelled by a component to the distance travelled by the solvent front) are as follows:

Au^{+3} = 1.0; Hg^{+2} = 0.90; Po^{+4} = 0.80; Pt^{+4} = 0.5; Tl^{+3} = 0.05; Bi^{+3} = 0.60; and Pb^{+2} = 0.00

8. The desired zones were 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 HCl and rinsed by downward percolation with H_2O.

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 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 per cent KI; (b) 1 per cent solution of diphenyl carbazide in alcohol; (c) 0.05 per cent solution of benzidine in 10 per cent acetic acid.

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.

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E. Lederer and M. Lederer, Chromatography, Elsevier Publishing Company, New York (1955).

Procedure X

SEPARATION OF POLONIUM, PROTACTINIUM OR MIXTURES THEREOF IN AQUEOUS SOLUTION FROM BISMUTH, LEAD, ZIRCONIUM AND/OR COLUMBIUM VALUES

Q. Van Winkle and K. A. Kraus (to U. S. Atomic Energy Commission).

U. S. Patent 2,910,345. Oct. 27, 1959

Source: Nuclear Science Abstracts, 14, 7467, (1960)

A process is presented for separating Po, Pa, or mixtures thereof in aqueous solution from Bi, Zr. Pb and Nb values contained in the solution. The method comprises providing HCl in the solution in a concentration of at least 5 N, contacting the aqueous solution with a substantially water-immiscible organic solvent such as diisopropyl ketone, and separating the aqueous phase containing the Bi, Zr, Pb and Nb from the organic extract phase containing Po, Pa, or mixture thereof.

Procedure XI

POLONIUM SEPARATION PROCESS

D. G. Karraker (to U. S. Atomic Energy Commission)

U. S. Patent 2,894,817. July 14, 1959

Source: Nuclear Science Abstracts, 14, 2494, (1960)

A liquid-liquid extraction process is presented for the recovery of Po from Pb and Bi. According to the invention an acidic aqueous chloride phase containing the Po, Pb, and Bi values is contacted with a tributyl phosphate ether phase. The Po preferentially enters the organic phase which is then separated and washed with an aqueous HCl solution to remove any Pb or Bi which may also have been extracted. The now highly purified Po in the organic phase may be transferred to an aqueous solution by extraction with aqueous HNO_3.

Procedure XII

PREPARATION OF POLONIUM METAL

Source: K. W. Bagnall, D. S. Robertson, J. Chem. Soc., 1044 (1957).

The Po is best precipitated from N HCl solution containing at least 100 mc/ml of Po^{210}; more dilute solutions should be concentrated by precipitation with $La(OH)_3$ before treatment with H_2S. The attempted precipitation of the Po from dilute solution (20 mc/ml) with lead carrier gave poor yields. The precipitated sulphide is "unwettable" and tends to float on the surface of the liquid and stick to the walls of the glass tube in which the precipitation is carried out; this is overcome by adding a little absolute alcohol or alcohol-toluene. The sulphide precipitate was filtered off on a No. 3 porosity filter stick mounted on a modified Buchner flask, washed with alcohol-toluene to remove sulphur, then sealed into a distillation tube of the type described earlier. **(See footnote on page 51.)**

The sulphide was decomposed by heating at 275° for 10 min., (5μ pressure) and the Po distilled at the same pressure by heating at 450-500° for 15 min.; the metal was then sealed off under vacuum until required. The filter sticks can be re-used a number of times. The micro-filter sticks described in an earlier paper* can be used for smaller (1 cc) preparations. The time required for the complete purification cycle is less than one hour and the overall recoveries at the curie level are in the range 96-99 per cent and depend on the precipitation efficiency, since the distillation efficiency is about 99.7 per cent. The method compares favorably with other procedures used for the purification of Po and it provides a very pure product.

Procedure XIII

TRACE EXTRACTION EXPERIMENTS

Source: French Hagemann, J. Amer. Chem. Soc., 72, 768 (1950)

Equal volumes (from 5-15 ml) of aqueous solutions containing radioactive tracers and 0.25 M benzene solutions of thenoyltrifluoro-acetone (TTA) were equilibrated by vigorous mechanical stirring for 15 min. at room temperature. The two phases were then allowed to separate and the pH of the aqueous phase measured with a Beckman glass electrode. Fifty or one hundred microliter aliquots of each phase were removed and evaporated upon Pt discs for radioactive assay. The pH of the solution was then adjusted by addition of NaOH or HCl and the procedure repeated until the range from zero to complete extraction had been covered.

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* Bagnall, D'Eye and Freeman, J. Chem. Soc., 2320 (1955).

Ionium was used as a tracer for Th, RaF for Po, RaE for Bi, $MsTh_2$ for Ac, Ra^{226} for Ra and Tl^{204} for Tl.

Some difficulty was encountered with Po and Bi in obtaining a material balance between the known concentration of added tracer and that determined by assay of the aliquots from each phase. It is probable that this was due to slow deposition of some of the activity upon the walls of the vessel as a result of hydrolysis. The difficulty was avoided by preparing a series of aqueous solutions pre-adjusted approximately to the desired pH, then adding the tracer and equilibrating with TTA solution. Aliquots were than immediately removed for assay and the equilibrium pH measured.

Reviewer's Note: The results of the above work were presented in the form of a graph. The following approximate values were obtained from that graph:

Element	pH for extracting		
	10%	90%	100%
Th	0.2	0.6	1.2
Po	0.4	1.3	2.4
Bi	1.5	2.0	3.0
Tl^{+3}	2.0	3.3	4.7
Pb	2.7	3.7	5.2
Ac	3.9	4.9	6.0
Tl^{+1}	4.9	6.5	8.0

Therefore, good separations of Po from Pb, Ac, and Tl can be achieved by this method. Poorer separations from Bi and Th could be obtained with proper control of pH.

PREFACE TO PROCEDURES XIV THROUGH XIX

The material in Procedures XIV through XIX was kindly submitted by Dr. Manfred Lindner, of the University of California, Livermore, California. It represents work performed by Dr. Lindner and Mr. Richard Nagle. The following remarks apply to all of the procedures:

The Po tracer used was Po^{206} made by irradiation of Pb foil with 48-Mev alpha particles of the 60-inch Berkley cyclotron. The course of the tracer in the experiments was followed by counting the samples in test tubes, in a well-type scintillation counter. The use of Po^{206} as a gamma tracer eliminated the inconvenience of alpha-counting small aliquots of each chemical fraction.

Unfortunately, the Po^{206} tracer decayed to Bi^{206}, (6 day half life) so that before an experiment, the latter had to be removed. This was achieved by maintaining the Po in a ketone medium and, just before use, removing the Bi^{206} by several equilibrations with 6 <u>N</u> HCl, though one such contact would have been sufficient. Sometimes, however, small amounts of Bi^{206} growth had to be reckoned with during the course of an experiment, and allusion is made to such instances.

Early in the experiments it was found that, for a fixed quantity of tracer, a "material balance" was difficult to achieve -i.e., being able to account for all of the tracer used in a given experiment. It was ultimately found that the Pt stirring wires were capable of taking up, perhaps by chemical plating, very considerable quantities of the tracer. Therefore, Pt wires were replaced by wires with a polyethylene sleeve. No such uptake of Po tracer was noticed under these conditions.

Procedure XIV

THE DISTRIBUTION OF PO TRACER BETWEEN HEXONE AND AQUEOUS SOLUTIONS

Source: M. Lindner, Private communication

In the following tests, approximately 25 lambda of Po tracer in hexone solution was added to several 1.0-ml portions of hexone. These were then equilibrated, using polyethylene-covered stirrers, with 1.0 ml of 6 N HCl for approximately 30 seconds. The layers were then centrifuged, and the entire 6 N HCl layer removed and placed in a counting tube. The hexone layers were then equilibrated with the aqueous solutions shown in columns 2-5 (in col. 5, the HCl-hexone mixture was saturated with H_2S for several minutes). After centrifugation, the layers were transferred to counting tubes. The emptied tubes in which the equilibrations were carried out were also counted. Results are shown in Table 1.

The losses to the glassware at low acid concentrations, especially in the case of dilute ammonium hydroxide, suggest hydrolysis and/or polymerization, followed by radiocolloidal adsorption. The distribution quotient does not seem in any case to greatly favor the aqueous phase.

Table 1

Sample \ Aqueous Phase	1 N H_2SO_4	Dilute NH_4OH	Water	6 N $HCl-H_2S$
6 N HCl layer	2,531	1,990	1,810	1,655
Aqueous layer	10,413	16,280	36,252	41,076
Hexone layer	49,496	7,546	18,358	15,797
Emptied tube	1,694	30,254	3,816	641
Total material balance	64,134	56,070	60,236	59,169
$K_d = \frac{\text{organic}}{\text{aqueous}}$	4.8	--	0.51	0.38
K_d for 6 N HCl	25	28	33	36

Other K_d measurements between H_2O and hexone, and 1 N H_2SO_4 and hexone failed to confirm the values found in Table 1; reproducible results could be obtained only in the case of 6 N $HCl-H_2S$. Water or solutions of low acidity were, therefore, not considered reliable for use in a separation scheme for Po.

Procedure XV

CARRYING OF Po^{206} ON Te METAL

Source: M. Lindner, Private communication.

About 50 lambda of purified Po^{206} tracer in hexone solution was added to duplicate 2.0-ml portions of HCl of the concentration shown in columns 2-5 in Table 2. The tubes were then heated to about 90°C for about a half-hour. Several milligrams of Te carrier were added to each tube. A few small crystals of $SnCl_2$ were added to each of the tubes in one set, while each tube in the other set was saturated with SO_2, first at 90°C, then again after cooling to nearly room temperature. After standing for about one hour, the tubes were centrifuged and the supernatant solutions and Te precipitates counted separately.

Table 2

Carrying of Po^{206} on Te^{o}

HCl	0.3	1.0	2.0	3.0	6.0
Te precipitated by SO_2					
Te^{o}	56,152	22,421	1,327	928	742
supn't	2,663	35,397	57,173	55,704	55,550
Total	58,815	57,818	58,500	56,632	56,292
Te precipitated by $SnCl_2$					
Te^{o}	57,470	58,458	57,024	55,866	54,611
supn't	570	673	511	930	2,624
Total	58,040	59,131	57,535	56,796	57,235

Thus, Po is nearly quantitatively carried (approximately 95 per cent from 6 N HCl) on Te reduced with $SnCl_2$. With SO_2 reduction, however, the non-carrying is essentially quantitative at [HCl] >2 N. These observations suggest a means of isolating Po tracer by first carrying on Te^o by reduction with $SnCl_2$, followed by separation of Te^o from Po by reduction with SO_2 gas at HCl concentrations above 2 N.

Procedure XVI

RE-EXTRACTION INTO HEXONE OF POLONIUM BACK-EXTRACTED FROM HEXONE INTO 6 N HCl - H_2S

Source: M. Lindner, Private communication

About 50,000 dpm of Po^{206} in approximately 50 lambda of hexone was added to a mixture of equal volumes of hexone and 6 N HCl. A stream of H_2S was passed through the mixture for several minutes. The aqueous layer was completely removed and the procedure repeated with the same volume of fresh 6 N HCl. The three layers were then counted.

Table 3

K_d for 6 N HCl - H_2S - Hexone System

Layer	dpm	K_d
1st HCl - H_2S	40,510	0.37
2nd HCl - H_2S	10,980	0.36
hexone	4,000	

The HCl - H_2S layers were then combined and boiled to a small volume to expel all H_2S. The solution was then made to the original volume with 6 N HCl. This solution was then twice equilibrated with hexone. The layers were then counted.

Table 4

K_d for 6 N HCl - Hexone System

Layer	dpm	K_d
1st organic	39,282	11.4
2nd organic	2,700	3.7
6 N HCl	734	

The second K_d cannot be taken too seriously in view of the growth of at least a small amount of Bi^{206} during the course of the experiment, which would ultimately be found in the 6 N HCl layer.

Although the first K_d is in disagreement with the apparent K_d of approximately 30 from Table 1, it appears that, in view of the crudeness of this type of experiment, the distribution between 6 N HCl and hexone favors the hexone by roughly an order of magnitude. The distributions between 6 N HCl-H_2S and hexone shown in Table 3 are in good agreement with each other, and also with the result in Table 1. This may be fortuitous.

The extraction behavior of Po in the presence and absence of H_2S suggests the following purification cycle: (a) extract Po into hexone, (b) back-extract three times into HCl-H_2S, (c) boil to expel the H_2S, (d) re-extract into hexone, and (e) back-extract into HCl-H_2S.

Procedure XVII

THE EXTRACTION OF Po INTO HEXONE FROM HCl-SO_2 SOLUTIONS FROM THE NON-CARRYING PRECIPITATION OF Te^o WITH SO_2 GAS

Source: M. Lindner, Private communication

In the following experiments the supernatant solutions from the SO_2 - precipitated Te^o at 1.0, 3.0, and 6.0 N HCl listed in Table 2 were equilibrated with equal volumes of hexone for about 10 seconds, the layers then being separated and counted. Results are shown in Table 5.

Table 5

Extraction of Polonium Into Hexone From SO_2-Saturated Solutions of HCl

Phase	1 N HCl	3 N HCl	6 N HCl
Aqueous	26,031	20,949	5,816
Hexone	8,024	34,122	50,259
K_d	0.31	1.63	8.6

It, therefore, appears that the presence of SO_2 has no "adverse" effect upon the extraction of Po into hexone. (This suggests that, following separation of Te from Po, the latter may be extracted directly into hexone for further purification.) The value K_d = 8.6 seems at variance with the values reported in Table I for 6 N HCl. In view of the growth of Bi^{206} during the

Equilibration of Phases from Column 4, Table 5

Starting Phase	Original Activity	Hexone After Equilib.	6 N HCl After Equilib.	K_d
Aqueous	5,816	3,386	2,778	1.22
Hexone	50,259	48,399	2,957	16.4

period in which this experiment was performed, both layers shown in column 4 in Table 5 were equilibrated with the opposite phase.

If it is assumed that the 2,778 c/m residual in the aqueous phase be due to Bi^{206}, then, the corrected K_d value for col. 4, Table 5 would be 16.6 instead of 8.6 -- a value in agreement with the K_d of 16.4 above, and not in too violent disagreement with either Table 1 or Table 4. For the elapsed time, this amount of Bi^{206} growth was not unreasonable.

Procedure XVIII

THE BEHAVIOR OF POLONIUM ON DOWEX-50 RESIN

Source: M. Lindner, Private communication.

Polonium was carried on Te and dissolved in conc. HNO_3. This was evaporated to the point of dryness and taken up in 0.2 $\underline{N}$ HCl. This was allowed to percolate through a column of Dowex-50X12 resin. Elution with 2 $\underline{N}$ HNO_3 removed all Te and Bi activities, and the Po was then successfully eluted with 2 $\underline{N}$ HCl. The Po yield was about 70 per cent. Thus, the observations reported by Bagnall (Reference 5, p. 21) were confirmed. Moreover, this behavior was reproducible.

However, if a solution of Po in 2 $\underline{N}$ HCl solution was diluted to 0.2 $\underline{N}$ HCl, the Po could not be made to adsorb on Dowex-50 at all. Yet, if the same solution were boiled to near-dryness and repeatedly fumed with conc. HNO_3 to remove all the chloride, followed by taking up the residue in 0.2 N HCl, the subsequent solution adsorbed "normally" upon Dowex-50.

Procedure XIX

THE BEHAVIOR OF POLONIUM ON DOWEX A-1 RESIN; COMPARISON WITH BISMUTH

Source: M. Lindner, Private communication.

Roughly 8 x 10^4 c/m of purified Bi^{206} tracer and 5 x 10^4 c/m of purified Po^{206} tracer were each heated for about 20 minutes in a hot-water bath with separate 1 ml slurries of Dowex A-1 X4 (50-100 mesh) in 6 N HCl. Tests of the supernatant liquids showed that in both cases the tracer adsorption was essentially complete. The slurried resins were then placed on top of a 3-inch x 4 mm column of 6 N HCl-washed Dowex-A-1X4 (50-100 mesh). Three milliliter volumes of the elutriants shown in col. 1 were passed through each column. The c/m eluted are shown in Table 6.

Thus, Bi^{206} tracer was rapidly eluted with 3 N H_2SO_4 but the Po behavior was rather indefinite with the eluting agents tested, and complete elution was never effected. This observation seems at variance with the results reported by Bagnall (Reference 5, p. 21) in which it is stated that elution is effected with 1 N HNO_3.

Table 6

Behavior of Bi^{206} and of Po^{206} Tracer on Dowex A-1

Elutriant	Bi^{206} c/m	Po^{206} c/m
1 N H_2SO_4	0	0
1 N "	0	35
3 N "	30,890	100
3 N "	44,420	234
3 N "	7,540	39
3 N	2,165	--
1 N HNO_3	complete	290
"	--	5
"	--	15
"	--	290
4 M $HClO_4$	--	4,120
"	--	2,490
"	--	1,802
8 M HNO_3	--	7,509
"	--	4,615
16 M HNO_3	--	3,170
"	--	3,460

Procedure XX

Source: A. Karl cited in K. W. Bagnall, "Chemistry of the Rare Radioelements" Academic Press Inc., New York, 1957

Polonium can be separated from Bi in very dilute HNO_3 solution by precipitation with lead tellurate; the solution of Po, Pb and Bi is heated with telluric acid and a precipitate of lead tellurate, which carries most of the Po, is formed on standing. The Pb is then eliminated by digesting the precipitate with H_2SO_4 and filtering off the insoluble $PbSO_4$. The filtrate is evaporated to dryness, the residue dissolved in conc. HCl and the resulting solution boiled to reduce the Te to the quadrivalent state. The Te can then be precipitated as the element by reduction with SO_2, leaving a comparatively pure solution of Po. Overall yields of about 97 per cent have been claimed for this procedure.

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