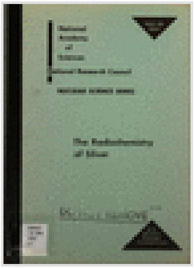

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The Radiochemistry of Silver

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Columbus, Ohio

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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 silver 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 authors any published or unpublished material on the radiochemistry of silver which might be included in a revised version of the monograph.

The Radiochemistry of Silver

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Battelle Memorial Institute
Columbus, Ohio

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

Pp. 99-104 in Volume I and pp. 49-52 and 646-649 in Volume II of "Analytical Chemistry", F. P. Treadwell, tr. and rev. by William T. Hall, John Wiley and Sons, Inc., New York, ninth edition, 1937.

Chapter 18, pp. 818-844 in "Inorganic Chemistry", T. Moeller, John Wiley and Sons, Inc., New York, 1952.

Pp. 204-209 in "Applied Inorganic Analysis", W. F. Hillebrand, G. E. Lundell, H. A. Bright, and J. I. Hoffman, John Wiley and Sons, Inc., New York, second edition, 1953.

Pp. 173-190 in "Prescott and Johnson's Qualitative Chemical Analysis", R. K. McAlpine and B. A. Soule, Van Nostrand, New York, 1933.

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF SILVER

"Evaluation of Radiochemical Separation Procedures", Duane N. Sunderman and W. Wayne Meinke, Analytical Chemistry 29, 1578, November 1957.

"The Development and Evaluation of Radiochemical Separation Procedures for Barium, Calcium, Strontium, Silver, and Indium", Duane N. Sunderman, AECU-3159, February 1956.

III. TABLE OF ISOTOPES OF SILVER

Isotope	Half Life	Primary Radiations		Method of Preparation
		Type of Decay	Gamma Rays	
Ag^{103}	59 min	β^+ 1.3 Mev EC	0.554 Mev 0.764	Cd^{106} (p, α)
Ag^{104}	27 min	β^+ 2.70	0.118 0.556	daughter of Cd^{104}
Ag^{105}	40 days	EC	0.064 0.281 0.345 0.443 0.654	Rh^{103}(α, 2n), Pd^{105}(p, n), Pd^{105}(d, 2n)
Ag^{106}	24 min	β^+ 1.95 1.45 β^- 0.36 ($\sim$1%) EC	0.512 (17%)	Rh^{103}(α, n), Pd^{105}(d, n)
Ag^{106}	8.3 days	EC	0.513 0.624 0.72 1.045 1.131 1.388 1.53	Ag^{107}(n, 2n), Pd^{106}(p, n), Rh^{103}(α, n)
Ag^{107m}	44 sec	IT 0.093	0.093	Daughter of Cd^{107}
Ag^{107}	Stable (51.35%)			
Ag^{108}	2.3 min	β^- 1.77 (97%) 1.1 (1%) β^+ (0.1%) EC (1.6%)	0.43 0.60 0.63	Ag^{107} (n, γ)
Ag^{109m}	40 sec	IT 0.088	0.088	Daughter of Pd^{109} and Cd^{109}, fission product
Ag^{109}	Stable (48.65%)			
Ag^{110m}	253 days	β^- 0.086 (63%) 0.536 (32%) IT 0.116 (5%)	0.116 0.656 0.575 0.619 0.677 0.705 0.764 0.884	Ag^{109} (n, γ)

III. TABLE (CONTINUED)

Isotope	Half Life	Primary Radiations		Method of Preparation
		Type of Decay	Gamma Rays	
			0.937 1.384 1.504	
Ag^{110}	24 sec	β^- 2.16 2.84	0.66	Daughter of Ag^{110m}
Ag^{111m}	74 sec	IT 0.087	0.087	Daughter of Pd^{111}
Ag^{111}	7.5 days	β^- 1.04 (91%) 0.70 (8%) 0.80 (1%)	0.243 (1%) 0.340 (8%)	Fission product, daughter of Pd^{111} and Pd^{111m}
Ag^{112}	3.2 hr	β^- 4.1 (25%) 3.5 (40%) 2.7 (20%) ~1 (15%)	0.618 1.39 1.62 2.11	Fission product, daughter of Pd^{112}
Ag^{113m}	1.2 min	$\beta^- < 2.0$	0.14 0.30 0.39 0.56 0.70	Daughter of Pd^{113}
Ag^{113}	5.3 hr	β^- 2.0	0.31 (weak)	Fission product
Ag^{114}	5 sec	β^- 4.6	0.57	Daughter of Pd^{114}
Ag^{114}	2 min	β^-		Fission product
Ag^{115m}	20 sec	β^-		Fission product
Ag^{115}	21 min	β^- 2.9	0.138 (weak) 0.227 (weak)	Fission product
Ag^{116}	2.5 min	β^- 5.0	0.70 0.52	Fission product
Ag^{117}	1.1 min	β^-		Fission product

For more complete information on the radiations of the isotopes of silver 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.

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

1. Metallic Silver

Silver is a white metal, having a density of 10.5 g/cc at 20 C, a melting point of 960.5 C, and a boiling point of 1950 C. It is a very malleable and ductile metal and is superior to all other metals in conduction of heat and electricity.

Silver is a noble metal and is easily reduced to the metallic state. Heat alone is sufficient to reduce silver oxide, carbonate, or cyanide. The addition of metals such as zinc, copper, or iron to a solution of silver ions will reduce the silver to the metal, as will formic acid, stannous chloride, and ferrous sulfate[1].

Electrolytic reduction of silver is easily accomplished, and purification of the metal is commonly brought about in this manner. Oxidation potentials of silver are given below[2]:

$Ag = Ag^{+} + e^{-}$ $\quad E^{\circ}_{298} = -0.7995$ V

$2Ag + 2OH^{-} = Ag_2O + H_2O + 2e^{-}$ $\quad E^{\circ}_{298} = -0.344$ V

$Ag^{+} = Ag^{+2} + e^{-}$ $\quad E^{\circ}_{298} = -1.98$ V

$Ag_2O + 2OH^{-} = 2\ AgO + H_2O + 2e^{-}$ $\quad E^{\circ}_{298} = -0.57$ V

$Ag^{+} + H_2O = AgO^{+} + 2H^{+} + 2e^{-}$ $\quad E^{\circ}_{298} =$ ca. -2.0 V

$Ag^{+2} + H_2O = AgO^{+} + 2H^{+} + e^{-}$ $\quad E^{\circ}_{298} =$ ca. -2.1V

$2AgO + 2OH^{-} = Ag_2O_3 + H_2O + 2e^{-}$ $\quad E^{\circ}_{298} = -0.74$ V

The most stable oxidation state is Ag(I). The Ag(II) state exists as the solid oxide and fluoride, in a number of complex compounds, and in strong oxidizing solutions[3]. The Ag(III) state exists in some complex compounds, in strong oxidizing solutions[4], and possibly as the solid oxide[5].

2. Soluble Salts of Silver

In aqueous solutions the only stable oxidation state of silver is the +1 state. The +2 and +3 silver ions are such powerful oxidizing agents that they are unstable in water solutions because of their reduction by water[6]. The soluble salts of silver include the nitrate, nitrite, fluoride, chlorate, perchlorate, bromate, sulfate, permanganate, acetate, and tartrate. The fluoride is the only soluble silver halide.

3. Insoluble Salts of Silver and Precipitation and Coprecipitation Characteristics of Silver

The conditions for gravimetric determinations of silver are well defined in standard analytical works[7,8,9]. Silver falls into group I of the qualitative analysis scheme. Table 1 lists the common insoluble compounds of silver and the reagents employed to precipitate them. Several of these compounds have been employed in radiochemical procedures, the most popular being the chloride and the sulfide.

TABLE 1. INSOLUBLE COMPOUNDS OF SILVER

Reagent	Precipitate	Solubility in Water, g/100 cc (25C)	Solubility in Other Reagents
Cl^-	AgCl	1.8×10^{-4}	Soluble in NH_4OH, Soluble in $Na_2S_2O_3$ or KCN solutions
Br^-	AgBr	1.3×10^{-5}	Soluble in $Na_2S_2O_3$ or KCN solutions, Slightly soluble in NH_4OH
I^-	AgI	2.8×10^{-7}	Insoluble in NH_4OH, Soluble in $Na_2S_2O_3$ or KCN solutions
NaOH or KOH solution	Ag_2O	2.1×10^{-3}	Soluble in NH_4OH, Soluble in KCN solution, Soluble in HNO_3
Fe, Zn, or Cu metal Fe^{++}, Sn^{++}, or $HCHO_2$	Ag	insoluble	Soluble in HNO_3 Soluble in hot, conc. H_2SO_4
H_2S or $C_2H_3OS^-$	Ag_2S	1×10^{-16}	Insoluble in NH_4OH, Soluble in hot, dilute HNO_3
$CrO_4^{=}$	Ag_2CrO_4	2.5×10^{-3}	Soluble in NH_4OH, Soluble in HNO_3
$Cr_2O_7^{=}$	$Ag_2Cr_2O_7$	8.3×10^{-3}	Soluble in NH_4OH, Soluble in HNO_3
$CO_3^{=}$	Ag_2CO_3	3.2×10^{-3}	Soluble in excess NH_4CO_3, Soluble in NH_4OH or $Na_2S_2O_3$ solution
$HPO_4^{=}$	Ag_3PO_4	6.5×10^{-4}	Soluble in NH_4OH, Soluble in HNO_3
$S_2O_3^{=}$	$Ag_2S_2O_3$	insoluble	Soluble in excess $Na_2S_2O_3$ solution Soluble in NH_4OH

(Table continues on following page.)

TABLE 1. (CONTINUED)

Reagent	Precipitate	Solubility in Water, g/100 cc (25C)	Solubility in Other Reagents
IO_3^-	$AgIO_3$	4.4×10^{-3}	Soluble in NH_4OH, Soluble in HNO_3
$C_2O_4^=$	$Ag_2C_2O_4$	3.5×10^{-3}	Soluble in NH_4OH, Soluble in KCN solution, Soluble in HNO_3
CN^-, acid	AgCN	2.3×10^{-5}	Soluble in NH_4OH, Soluble in HNO_3, Soluble in excess KCN or in $Na_2S_2O_3$ solution
benzotriazole ($C_6H_4N_3H$)	$AgC_6H_4N_3$	insoluble	Soluble in conc. mineral acids, Soluble in KCN or $Na_2S_2O_3$ solution

Chloride. The use of a chloride precipitation to separate silver from other radioisotopes or to obtain the silver in a form suitable for weighing and counting has been reported extensively in the literature[10-38]. The popularity of this method is due mainly to the fact that few other elements are precipitated under the conditions of a silver chloride precipitation.

The most common method of precipitating silver chloride is the addition of hydrochloric acid to a dilute nitric acid solution of the silver. Occasionally the solution is heated to promote coagulation or a wetting agent such as aerosol is added to prevent the precipitate from sticking to the sides of the vessel. A large excess of chloride ions should be avoided, for silver forms a soluble chloride complex, $AgCl_3^=$.[7] One liter of 1 per cent HCl dissolves only 0.0002 g of AgCl at 21C, but 1 liter of 5 per cent HCl dissolves 0.0003 g, and 1 liter of 10 per cent HCl dissolves 0.0555 g[39].

The AgCl precipitate is readily dissolved in dilute ammonia and reprecipitated by addition of nitric acid, with no loss in yield[31]. This is very useful in improving the radiochemical purity of silver in separations from other activities[12,13,20,24]. The ammonia complex of silver, formed when silver chloride is dissolved in ammonia, may also be destroyed by volatilization of the ammonia[40]. This has been employed by Firsching to selectively precipitate the silver halides[41]. He found that when a solution of the $Ag(NH_3)_2^+$ complex and iodide, bromide, and chloride ions is heated to volatilize ammonia and lower the pH, AgI precipitates at pH 10, AgBr at pH 8.5, and AgCl at pH 7. The ammonia complex has also been destroyed by addition of beta-hydroxyethyl acetate to a solution of the complex and chloride ions[42]. The hydrogen ions released as the beta-hydroxyethyl acetate hydrolyzes destroy the complex and AgCl precipitates.

Silver chloride has also been precipitated by dilution of a solution of the silver chloride complex[19,24] and by releasing chloride ions by hydrolysis of ethylene or propylene chlorohydrin[42]. In the latter method the chlorohydrin is heated at 60 C with a solution of the silver. Complete precipitation of the AgCl requires several hours of heating, as the chloride is released very slowly.

The contamination of silver chloride precipitates by thirteen typical tracer activities has been studied[31,32]. The experimental conditions employed in the study were as follows: 10 mg of silver carrier and 10 mg of carrier and tracer for the interfering element were mixed and diluted to 10 ml with 1M nitric acid, 0.1 ml of concentrated hydrochloric acid was added with stirring, the precipitate was digested for five minutes at room temperature, and it was then separated by centrifuging. The percentage of each element carried with the AgCl precipitate is given in Table 2. The yield for the silver chloride was 99 ± 1.3 per cent. The quantitative precipitation of iodine with the silver was expected, as AgI is more insoluble than AgCl. A high percentage of antimony contaminated the AgCl. Antimony is difficult to keep in solution during any change in acidity, particularly when a precipitate is being formed, and SbOCl often precipitates with AgCl. The other interferences which stand out are those of the platinum group, iridium and ruthenium. This is consistent with the fact that multiple precipitations are necessary to separate silver from irradiated palladium since a large portion of the palladium is carried on the early precipitations. This difficulty in separating silver from palladium by precipitation of AgCl has also been experienced with fission product solutions[20]. The presence of zirconium carrier was observed to retard the precipitation of the AgCl and prevent it from being quantitative[31,32].

TABLE 2. CONTAMINATION OF SILVER PRECIPITATES BY OTHER ACTIVITIES[31,32]

	Per Cent Carried(a)	
Tracer	Chloride (Carrier Added)	Benzotriazole (Carrier Added)
Ag^{110}(b)	99 ± 1.3	92 ± 5
Ce^{144}, Pr^{144}	0.5	2.3
Co^{60}	0.5	2.5
Cr^{51}	0.5	92
Cs^{134}	0.5	2.4
I^{131}	97	98
Ir^{192}	27	29
Ru^{106}, Rh^{106}	2.5	2.5
Sb^{124}	22	52
Se^{75}	0.5	2.7
Sn^{113}, In^{113m}	0.8	77
Sr^{90}, Y^{90}	0.7	2.4
Ta^{182}	0.6	87
Zr^{95}, Nb^{95}	0.4	3.9

(a) Average of duplicate runs except for silver.

(b) Average of quadruplicate runs. Errors are "standard deviations".

The yield data applies only to the experimental conditions described in the text.

Bromide. The use of a silver bromide precipitation has been very limited in the radiochemistry of silver, bit it has been employed in bromine separations to obtain a form suitable for weighing and counting[43,44]. Ruka and Willard determined the solubility of silver bromide by mixing dilute solutions of silver nitrate and potassium bromide labelled with Br^{82} tracer[45]. The precipitates were almost invisible. The solubility is only 0.13 mg per liter.

Iodide. Precipitation of silver iodide has been used to a small extent in the radiochemistry of silver[14,33,46]. It has been employed more extensively in radiochemical separations of iodine[47-49]. Silver iodide is usually precipitated by addition of hydriodic acid or sodium or potassium iodide to a solution of silver ions. A milky suspension and large clumps of precipitate tend to form; so the precipitate should be digested by gentle boiling and brisk stirring[46,49]. The silver iodide precipitate is practically insoluble in ammonia, but it dissolves in cyanide or thiosulfate solutions[1]. Silver iodide precipitates from ammonia solutions as the pH is reduced to 10 by evolving the ammonia[41].

Benzotriazole. Radiochemical separations of silver by precipitation with benzotriazole are satisfactory only in the presence of large quantities of a complexing agent, such as Versene in ammoniacal solution, to prevent the precipitation of many normally insoluble hydrous oxides[31,32]. Under these conditions, according to Cheng, chloride, bromide, fluoride, sulfate, nitrate, phosphate, and acetate do not interfere; iodide forms a less soluble precipitate, while cyanide and thiosulfate dissolve the precipitate and prevent precipitations; copper (II), iron (III), nickel (II), cadmium (II), zinc (II), and cobalt (II) do not interfere, while tin, antimony, titanium, and beryllium precipitate as hydrous oxides unless tartrate is present; and the iron (II) Versenate reduces silver to the metal[50]. In the absence of Versene benzotriazole precipitates copper (II), iron (II), nickel(II), cadmium (II), zinc (II), and cobalt (II).

The contamination of silver benzotriazole precipitates by thirteen typical tracer activities has been studied[31,32]. The following precipitation procedure was employed in this study: Ten mg of carrier and tracer for the interfering element were added to 10 mg of silver carrier, the solution was diluted to 5 ml with water, 5 ml of a 40 per cent solution of Versene in ammonia was added, 1 ml of 2.5 per cent benzotriazole solution in ammonia was added, and the precipitate was stirred and digested at room temperature for 5 minutes and centrifuged. The yield and contamination data are given in Table 2. The silver yield was only 92 per cent, due primarily to the slowness of precipitation and coagulation in the highly salted solution[32]. The bulky character of the precipitate caused it to adhere to the sides of the centrifuge cone and made the transfer of the precipitate difficult.

The limit of specificity of the silver benzotriazole precipitation is illustrated by the fact that large quantities of antimony, chromium, iodine, iridium, tantalum, and tin are carried with the silver. A separation is possible, however, from cerium, cesium, cobalt, ruthenium, selenium, strontium, and zirconium. A precipitation has also been performed from 0.1 M chloride solution, and no detectable chloride remained with the precipitate after washing once with water[32].

Sulfide. Silver sulfide precipitations have been employed in numerous radiochemical procedures for silver[10,11,17,19,21,22,25,28,29,34,37,38]. Hydrogen sulfide precipitates Ag_2S from neutral, ammoniacal, and acid solutions[1]. Silver sulfide is insoluble in ammonia or dilute potassium cyanide solution, but it is slightly soluble in concentrated potassium cyanide. It dissolves readily in hot, dilute nitric acid. Ammonium sulfide has also been used to precipitate Ag_2S from ammoniacal solutions[21,25].

Flaschka reports precipitation of Ag_2S by thioacetamide in ammoniacal or neutral solution[51]. The thioacetamide hydrolyzes to give H_2S. In sulfuric acid, the Ag_2S precipitates only with heating, and in the presence of small quantities of nitric acid sulfur forms first and then the Ag_2S precipitates.

Silver sulfide may also be precipitated from acid solution by ammonium thioacetate and from boiling dilute acid solutions by sodium thiosulfate[1].

Iodate. Silver iodate has found very limited use in radiochemistry, but its precipitation with HIO_3 or KIO_3 solution has been employed in at least two procedures[25,52]. The $AgIO_3$ may be dissolved in ammonia and reprecipitated by the addition of sulfuric acid[25].

Oxide. When alkali hydroxides are added to a solution of silver ions, brown Ag_2O is precipitated. Silver oxide is soluble in ammonia, nitric acid, or sulfuric acid. This precipitation has found some utility in radiochemistry[24,25,52]. It is particularly useful when the desired final form of the silver is a solution of silver nitrate[24]. The Ag_2O can be dissolved in nitric acid to yield a silver nitrate solution.

Chemical Reduction. Precipitation of silver metal by chemical reduction of the silver ions has been employed in a few radiochemical procedures[27,33,46,53]. Silver (I) may be reduced to the metal with formic acid, ferrous sulfate, stannous chloride, and metallic zinc[1]. Other metals higher in the potential series than silver or other reducing agents may be employed. Ascorbic acid has been used in an analytical procedure for determining silver[54]. Silver metal is precipitated by adding freshly prepared ascorbic acid solution (2 g per 100 ml) to silver nitrate solution heated nearly to boiling. Rouser and Hahn used this procedure to obtain a quantitative separation of silver from irradiated palladium[53].

Radiocolloid. The radiocolloidal properties of silver in trace concentrations have been utilized in a carrier-free separation of Ag^{111} from irradiated palladium[55]. The carrier-free silver is considered to agglomerate in basic solution, and it may be filtered or centrifuged. Schweitzer and Nehls report that 80 per cent of the Ag^{111} is recovered free of palladium by filtering the solution (at pH 11) through Whatman No. 50 filter paper[55]. A coagulation time of one hour is required before filtration. The Ag^{111} is removed from the paper by rinsing with dilute nitric acid. The same authors report that greater than 95 per cent yields are obtained by centrifuging the solution at pH 11.

Iron Hydroxides as Carriers for Silver. Silver does not coprecipitate to any great extent with ferric hydroxide in ammonia solution. When 10 mg of Fe (III) is precipitated as the hydrous oxide from 10 ml of solution with ammonium hydroxide, 91.4 per cent of the silver remains in solution in the absence of silver carrier[31,32]. In the presence of 10 mg of silver carrier, 91.3 per cent of the silver remains in solution[31,32].

A ferric hydroxide scavenge has thus been employed frequently to assist in the purification of silver[11,17,20-22,52].

The coprecipitation of trace quantities of silver as silver iodide, with ferric hydroxide has been reported[56]. This procedure was employed in a radiometric method of determining small quantities of silver with radioactive iodine[56]. Complete coprecipitation of silver with ferrous hydroxide has been reported[57]. The precipitation of the Fe (II) is carried out at pH 8 to 8.5 with ammonium hydroxide[57].

Lanthanum Hydroxide as a Carrier for Silver. Lanthanum hydroxide is an effective carrier for many elements, but very little silver is coprecipitated with this scavenger when ammonia is used[31,32]. When 10 mg of lanthanum is precipitated as the hydroxide from 10 ml of solution with ammonium hydroxide, 96.5 per cent of the silver remains in solution in the absence of silver carrier, and 97.3 per cent remains in solution in the presence of carrier[31,32].

Tellurium as a Carrier for Silver. Trace amounts of silver are coprecipitated with tellurium, probably as silver telluride[58]. Virtually complete precipitation of the silver is obtained when one mg of tellurium carrier is precipitated from a 2 N hydrochloric acid solution of the silver with stannous chloride. Higher chloride concentrations have an unfavorable effect on the yield. The silver is recovered by dissolving the tellurium precipitate in nitric acid. Microgram quantities of silver can be separated from iron, cobalt, nickel, and zinc by this method, but copper interferes somewhat[58].

Mercurous Chloride as a Carrier for Silver. The coprecipitation of silver with mercurous chloride has been employed in radiochemical separations of trace amounts of silver from palladium and other platinum group metals[59,60]. In one procedure 0.5 ml of a saturated solution of mercurous nitrate was added to 500 ml of 0.5 N hydrochloric acid which contained the silver. The resulting mercurous chloride precipitate contained more than 95 per cent of the silver[59]. In the other procedure the precipitation was performed by adding 100 mg of mercurous nitrate and dilute hydrochloric acid to a nitric acid solution of the silver[60]. The mercury can be removed from the silver either by volatilization[59] or by oxidation to Hg (II) with nitric acid and extraction into ethyl acetate[60].

4. Inorganic Complexes of Silver

Silver forms a number of inorganic complexes in solution, and some of them have been very useful to radiochemists. The formation of the $Ag(NH_3)_2^+$ complex has been employed in redissolving AgCl precipitates[10-13,17,21,22,24,52], and $AgIO_3$ precipitates[25,52] in ammonium hydroxide. The AgCl or $AgIO_3$ is readily reprecipitated from these solutions by acidification with no loss in yield. The formation of chloride complexes of silver in strong hydrochloric acid has been utilized to dissolve AgCl precipitates[19]. The AgCl is reprecipitated by dilution of the acid.

The inorganic complexes of silver are listed in Table 3. The formation constants reported for each complex are also given.

5. Organic Complexes of Silver

In Table 4 an extensive list is given of the organic liquids which form complexes with silver. The formation constants are for the 1:1 complexes, unless otherwise indicated.

6. Extraction of Silver Into Organic Solvents

No radiochemical procedures based on the solvent extraction of silver were found. There is, however, a limited amount of information available on the extractability of silver in various systems, and a few of these extractions might be applied to radiochemical separations.

Dithizone - The dithizone complex of silver is quantitatively extracted from dilute acid solutions into carbon tetrachloride or chloroform[61-64]. A number of other metals also extract, and the order of extractability is $Pd > Ag > Hg(II) > Cu(II) > Bi \geq Pt(II) > Tl(III) > Fe(II) > Sn(II) \geq Co \geq Ni > Zn \geq Pb > Mn > Cd$.[64] Metals such as Pd, Ag, Hg, and Cu may be extracted from dilute acid (0.1-0.5 N), but Cd requires a strongly alkaline solution.

(Text continues on page 20.)

TABLE 3. INORGANIC COMPLEXES OF SILVER

Complexing Agent	Reaction Product	Log K	References
NH_3	$AgNH_3^+$	3.37	a
	$Ag(NH_3)_2^+$	7.21	a
Cl^-	$AgCl$	3.41	b
	$AgCl_2^-$	5.29	b, c, d
	$AgCl_3^{-2}$	5.24	b
Br^-	$AgBr$	4.68	b
	$AgBr_2^-$	7.66	b
	$AgBr_3^{-2}$	8.51, 8.87, 9.03	b, e, f
	$AgBr_4^{-3}$	7.2, 9.2	b, e
	$AgBr_5^{-4}$	9.37	f
	$Ag_2Br_6^{-4}$	20	e
I^-	AgI	6.59	b
	AgI_2^-	11.74	b
	AgI_3^{-2}	13.68	b
	AgI_4^{-3}	13.9	b
IO_3^-	$AgIO_3$	0.6	g
	$Ag(IO_3)_2^-$	1.9	g
CN^-	$Ag(CN)_2^-$	21.4	h
	$Ag(CN)_3^{-2}$	21.8	i, j
	$Ag(CN)_4^{-3}$	20.6	i, j
SCN^-	$Ag(SCN)_2^-$	7.57	k
	$Ag(SCN)_3^{-2}$	9.08	k
	$Ag(SCN)_4^{-3}$	10.08	k
NO_2^-	$Ag(NO_2)_2^-$	2.7	l
$S_2O_3^{-2}$	$AgS_2O_3^-$	8.82	m
	$Ag(S_2O_3)_2^{-3}$	13.46, 12.78	m, n
	$Ag(S_2O_3)_3^{-5}$	13.06	n
SO_3^{-2}	$AgSO_3^-$	5 to 6	o
	$Ag(SO_3)_2^{-3}$	8.68	o
	$Ag(SO_3)_3^{-5}$	9	o
OH^-	$AgOH$	4.22	h
	$Ag(OH)_2^-$	3.64	h
$SeCN^-$	$Ag(SeCN)_2^-$	10.7	h
	$Ag(SeCN)_3^{-2}$	13.9	h
N_3^-	AgN_3	2.49	h
	$Ag(N_3)_2^-$	4.2	h
	$Ag(N_3)_3^{-2}$	3.90	h
	$Ag(N_3)_4^{-3}$	3.67	h
NO_3^-	$AgNO_3$	-0.3	h
SO_4^{-2}	$AgSO_4^-$	0.23	h
TeO_4^{-2}	$AgTeO_4^-$	0.36	h
ClO_3^-	$AgClO_3$	0.22	h
S^{-2}	AgS^-	5.28	p

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TABLE 4. ORGANIC COMPLEXES OF SILVER

Ligand	Log K	References
Quinoline	1.84 3.67*	a d
Pyridine	2.0 4.1*	a, b b
Alpha-Picoline	2.3 4.68*	a, d d
Beta-Picoline	2.00, 4.35*	d
Gamma-Picoline	2.3 4.70*	a, d d
p-Nitroaniline	0.8 1.6*	a d
m-Nitroaniline	0.85 1.7*	a d
Beta-Naphthylamine	1.62 3.23*	a d
Aniline	1.59, 1.44 3.17*	a, d d
Beta-Methylethylamine	3.17	a
Benzylamine	3.57, 3.29 7.14*	a, d d
Methylamine	3.34 6.68*	a d
Ethylamine	3.65, 3.30 7.14*	a, d d
n-Butylamine	3.74, 3.43 7.48*	a, d d
Isobutylamine	3.62, 3.38 7.24*	a, d d
1,3-Diaminopropane	2.55	d
1,2,3-Triaminopropane	5.6	a
Alanine	4.86	a
Glycine	3.51 6.89*	d a, d
Glycylglycine	2.72 5.0*	d a, d
1,3-Propane diamine	5.92	c
1,4-Butanediamine	5.67	c
1,3-Diamino-2-propanol	5.64	c

TABLE 4. (CONTINUED)

Ligand	Log K	References
Crotonaldehyde	-0.72	d
Crotonic acid	-1.04	d
Propyl cyanide (butyronitrile)	0.94	d
2-Methylallyl alcohol	1.04	d
1-Methylallyl alcohol	1.15	d
Crotyl alcohol	0.71	d
Piperazine	3.4	d
Diethylamine	2.98, 6.2*	d
2,2'-Diaminodiethylamine	6.1	d
Thiodiacetic acid	2.7, 6.32*	d
(Ethylthio) acetic acid	4.1, 7.25*	d
Morpholine	2.25, 4.92*	d
2,2'-Dihydroxydiethylamine	2.69, 5.48*	d
Tris(hydroxymethyl)methylamine	3.09, 6.56*	d
2,2'-Diaminodiethyl sulphide	8.18	d
2-Amino-2'-hydroxydiethyl sulphide	4.69, 8.73*	d
Pent-2-ene	1.80	d
2-Aminopyridine	2.86, 5.75*	d
3-Aminopyridine	2.17, 5.21*	d
4-Aminopyridine	2.80, 6.20*	d
2-Methylbut-2-en-1-ol	0.70	d
Ethylvinylcarbinol	1.15	d
Piperidine	3.16, 6.61*	d
Thiourea	13.1**	d
Oxalic acid	approximately 0	d
Methyl cyanide (acetonitrile)	1.2	d
Acetic acid	0.73, 0.64*	d
Dimethylamine	5.91*	d
Ethylenediamine	approximately 6, 7.4*	d
Chloroacetic acid	0.64, 0.53*	d

(Table continues on following page.)

TABLE 4. (CONTINUED)

Ligand	Log K	References
Ethanolamine	3.13, 6.68*	d
Acetone	-0.85	d
Allyl Alcohol	1.08, 1.56*	d
Allyl Amine	7.17*	d
n-Propylamine	7.68*	d
Trimethylamine	3.11*	d
2-Methoxyethylamine	2.95, 6.34*	d
2-Methylthioethylamine	4.17, 6.88*	d
Isobutene	1.79	d
Succinonitrile	1.0	d
1,5-Diaminopentane	5.95	d
1,3-Diamino-2,2-dimethylpropane	4.66	d
Furfurylamine	2.64, 5.98*	d
2-Thienylmethylamine	2.87, 6.51*	d
Methylenebisthio (acetic acid)	4.7, 6.5*	d
Cyclohexene	2.28	d
3-Cyanopyridine	2.90*	d
4-Cyanopyridine	3.08*	d
Phenol	0.34	d
Triethylenediamine	1.65	d
Hexamethylenetetramine	3.58	d
Triethylamine	2.6, 4.76*	d
2,2',2''-Triaminotriethylamine	7.8	d
NN'-Di-(2-aminoethyl)ethylenediamine	7.7	d
Nicotinamide	3.22*	d
Isonicotinamide	3.01*	d
3-Methoxypyridine	1.58, 3.67*	d
4-Methoxypyridine	2.28, 4.44*	d
Histidine	7.37	d
Thiodipropionic acid	2.9, 6.71*	d
Ethylenebisthiodiocetic acid	6.5, 10.41*	d

TABLE 4. (CONTINUED)

Ligand	Log K	References
Triethanolamine	2.30, 3.64*	d
1,2-Di-(2-aminoethylthio)ethane	5.08	d
Toluene	0.42	d
Benzoic acid	0.519, 0.556*	d
o-Toluidine	1.51	d
m-Toluidine	1.47	d
p-Toluidine	1.56, 3.48*	d
N-Methylaniline	1.00	d
2,4-Lutidine	2.59, 2.47 5.18*	a, d d
n-Heptylamine	approximately 2.7, 7.93*	d
Methyl nicotinate	2.99*	d
Methyl isonicotinate	2.45*	d
Trimethylenedithioacetic acid	approximately 5.7, 8.09*	d
Styrene	1.26	d
3,5-Xylidine	1.63	d
2,6-Xylidine	1.62	d
s-Collidine	4.75*	d
(Phenylthio)acetic acid	7.27*	d
gamma-Thiodibutyric acid	approximately 4, 7.00*	d
Tetramethylenedithiodiacetic acid	6.00, 8.36*	d
n-Propylbenzene	0.46	d
Isoquinoline	3.89*	d
(Benzylthio)acetic acid	7.13*	d
Pentamethylenedi(thioacetic acid)	6.3, 8.85*	d
Naphthalene	0.505	d
2,2'-Dipyridyl	6.8*	d
beta-(Benzylthio)propionic acid	7.34*	d
Ethylenediamine tetraacetic acid (EDTA)	7.32	d
Hexamethylenedithiodiacetic acid	6.0, 8.55*	d

(Table continues on following page.)

TABLE 4. (CONTINUED)

Ligand	Log K	References
Acridine	4.41*	d
trans-Stilbene	0.80	d
3-Methylcholanthrene	0.52	d

* Formation constant for AgA_2.
** Formation constant for AgA_3.

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In the procedure described by Friedeberg a 0.00005 M solution of dithizone in carbon tetrachloride is used to extract trace quantities of silver from an acid solution at a pH of about 2 in the absence of chloride.[61] If the chloride concentration is not over one per cent, a pH of 3.5 is used. If an ammonium chloride concentration as high as 20 per cent is present, the extraction is still quantitative at pH 5. Above a pH of 5 an enol form of the silver-dithizone complex forms, which is insoluble in carbon tetrachloride. The silver may be back extracted into chloride or thiocyanate solutions.

A masking agent such as EDTA is effective in preventing the extraction of Cu, Bi, Cd, Zn, and Pb but not mercury or silver.[63,64] Separation of silver from mercury and copper is accomplished by back extracting the silver into a mixture of equal volumes of 20 per cent NaCl and 0.03 N HCl. The copper and mercury remain in the organic phase.[64]

Sodium Diethyldithiocarbamate - Almost two dozen metals may be extracted into carbon tetrachloride or ethyl acetate with this reagent.[64-66] By using EDTA as a masking agent, however, the selectivity may be improved. The metals extracting are Ag, Cu, Fe, Co, Bi, Ni, Pb, U (VI), Cd, Mn, V, Zn, Cr (VI), Te (IV), Mo (VI), Ga, Tl, Nb (V), Re, Os, Se, Hg, As (III), Sb (III), Sn (IV). In, and W.[64,65]

An aqueous solution of the sodium diethyldithiocarbamate is added to the sample at a pH between 4 and 11, carbon tetrachloride is added, and the mixture is shaken to extract the silver.[64,66] A pH of 3 was reported for the extraction of silver into ethyl acetate with the diethyldithiocarbamate reagent.[65]

Dithio-beta-isoindigo - Small amounts of silver (5-10 mg) have been quantitatively extracted from a silver-lead solution into a solution of dithio-beta-isoindigo in n-butanol.[64,67] The lead remains behind in the aqueous phase.[64]

Triiso-octyl thiophosphate - The extraction of silver from nitric acid solutions into solutions of triiso-octyl thiophosphate (TOTP) in carbon tetrachloride has been reported.[68] The partition coefficient for the silver increases with both the nitric acid and the TOTP concentrations. From 6 M nitric acid and for a 0.67 M solution of TOTP in carbon tetrachloride, the partition coefficient exceeds 100 at room temperature. Of the 35 metals tested by the authors, the only other one having a high partition coefficient under the same conditions is mercury.[68] The silver may be stripped from the organic phase with dilute alkali or ammonia.

Tri-n-butyl thiophosphate - Tri-n-butyl thiophosphate (TBPS) in carbon tetrachloride has also been reported to be a selective extractant for silver and mercury.[68] The extraction behavior of this reagent is very similar to that of the TOTP discussed above.

7. Ion Exchange Behavior of Silver

Ion exchange like solvent extraction, has been used infrequently for radiochemical separations of silver. This is probably due to the high selectivity of such well-established procedures as isotopic exchange, electrodeposition, and precipitation.

Cation Exchange. Bonner and his coworkers have presented data on the adsorption of a number of cations, including silver, on Dowex-50.[69,70] Their selectivity scale relative to the lithium ion as unity is given in Table 5. The higher the number for a cation, the stronger is its affinity for Dowex-50.

TABLE 5. RELATIVE ADSORPTION OF CATIONS ON DOWEX-50[69,70]

	Per Cent Cross-Linkage		
Cation	4%	8%	16%
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	8.51	22.9
Tl^+	6.71	12.4	28.5
UO_2^{+2}	2.36	2.45	3.34
Mg^{+2}	2.95	3.29	3.51
Zn^{+2}	3.13	3.47	3.78
Co^{+2}	3.23	3.74	3.81
Cu^{+2}	3.29	3.85	4.46
Cd^{+2}	3.37	3.88	4.95
Mn^{+2}	3.42	4.09	4.91
Be^{+2}	3.43	3.99	6.23
Ni^{+2}	3.45	3.93	4.06
Ca^{+2}	4.15	5.16	7.27
Sr^{+2}	4.70	6.51	10.1
Pb^{+2}	6.56	9.91	18.0
Ba^{+2}	7.47	11.5	20.8
Cr^{+3}	6.6	7.6	10.5
Ce^{+3}	7.5	10.6	17.0
La^{+3}	7.6	10.7	17.0

Strelow has published a selectivity scale for 43 cations on sulfonated polystyrene AG50W-X8, which is processed from Dowex-50 by the Bio-Rad Laboratories of Berkeley, California.[71] This scale is based on the equilibrium distribution coefficient, K_d, where

$$K_d = \frac{\text{amount of ion on resin x volume of water phase, ml}}{\text{amount of ion in water phase x weight of dry resin}}.$$

This coefficient changes with compositions and concentrations of the reagents in the aqueous phase, the nature of the resin, and the ratio of the amount of cation to amount of resin in the system. Strelow's values for a hydrochloric acid system are given in Table 6. The values of K_d for silver, in addition to Hg^+, Pb^{+2}, Tl^+, and Hg^{+2}, were determined in nitric acid. To obtain an estimate of the volume of the eluting agent required to elute the maximum of the elution peak, the following equation may be employed:[71]

$$\bar{V} = K_d \text{ x (Mass of dry resin in the column)}$$

J. S. Fritz and his coworkers have studied the elution of metal ions from Dowex-50 with hydrofluoric acid.[72] Silver was one of the cations

TABLE 6. EQUILIBRIUM DISTRIBUTION COEFFICIENTS, K_d, FOR 43 CATIONS IN HYDROCHLORIC ACID USING THE SULFONATED POLYSTYRENE AG50W-X8 RESIN[71]

Cation	HCL Concentration 0.1 N	0.2 N	0.5 N	1.0 N	2.0 N	3.0 N	4.0 N
ZrO^{+2}	$>10^5$	$>10^5$	$\sim 10^5$	7250	489	61	14.5
Th^{+4}	$>10^5$	$>10^5$	$\sim 10^5$	2049	239	114	67
La^{+3}	$>10^5$	10^5	2480	265.1	48	18.8	10.4
Ce^{+3}	$>10^5$	10^5	2460	264.8	48	18.8	10.5
Y^{+3}	$>10^5$	$>10^4$	1460	144.6	29.7	13.6	8.6
Ba^{+2}	$>10^4$	2930	590	126.9	36	18.5	11.9
Hg^{+a}	$>10^4$	7600	640	94.2	33	19.2	13.6
Al^{+3}	8200	1900	318	60.8	12.5	4.7	2.8
Sr^{+2}	4700	1070	217	60.2	17.8	10.0	7.5
Ga^{+3}	$>10^4$	3036	260	42.58	7.75	3.2	0.36
Ca^{+2}	3200	790	151	42.29	12.2	7.3	5.0
Pb^{+2a}	$>10^4$	1420	183	35.66	9.8	6.8	4.5
Fe^{+3}	9000	3400	225	35.45	5.2	3.6	2.0
Cr^{+3}	1130	262	73	26.69[b]	7.9	4.8	2.7
Tl^{+a}	173	91	41	22.32	9.9	5.8	3.3
Ni^{+2}	1600	450	70	21.85	7.2	4.7	3.1
Co^{+2}	1650	460	72	21.29	6.7	4.2	3.0
Mg^{+2}	1720	530	88	20.99	6.2	3.5	3.5
Mn^{+2}	2230	610	84	20.17	6.0	3.9	2.5
Fe^{+2}	1820	370	66	19.77	4.1	2.7	1.8
Cs^{+1}	182	99	44	19.41	10.4	--	--
UO_2^{+2}	5460	860	102	19.20	7.3	4.9	3.3
Ag^{+a}	156	83	35	18.08	7.9	5.4	4.0
Cu^{+2}	1510	420	65	17.50	4.3	2.8	1.8
Hg^{+2a}	4700	1090	121	16.85	5.9	3.9	2.8
Zn^{+2}	1850	510	64	16.03	3.7	2.4	1.6
Rb^{+}	120	72	33	15.43	8.1	--	--
K^{+}	106	64	29	13.87	7.4	--	--
Be^{+2}	255	117	42	13.33	5.2	3.3	2.4
Ti^{+4}	$>10^4$	297	39	11.86	3.7	2.4	1.7
V^{+4}	--	230	44	7.20	--	--	--
Na^{+}	52	28.3	12	5.59	3.6	--	--
Li^{+}	33	18.9	8.1	3.83	2.5	--	--
Sn^{+4}	$\sim 10^4$	45	6.2	1.60	1.2	--	--
Cd^{+2}	510	84	6.5	1.54	1.0	0.6	--
V^{+5}	13.9	7.0	5.0	1.10	0.7	0.2	0.3
Mo^{+5}	10.9	4.5	0.3	0.81	0.2	0.4	0.3
Se^{+4}	1.1	0.6	0.8	0.63	1.0	--	0.7
Bi^{+3}	Ppt.	Ppt.	<1.0	1.0	1.0	1.0	1.0
As^{+3}	1.4	1.6	2.2	3.81	2.2	--	--
Sb^{+3}	Ppt.	Ppt.	Ppt.	Ppt.	2.8	--	--
Pt^{+4}	--	--	--	1.4	--	--	--
Au^{+3}	0.5	0.1	0.4	0.84	1.0	0.7	0.2
Hg^{+2}	1.6	0.9	0.5	0.28	0.3	0.2	0.2

a. Done in nitric acid.

b. More than one cationic species present.

which was not eluted with either 0.1 $\underline{M}$ or 1.0 $\underline{M}$ HF. This is not surprising since the fluoride complex of silver is not very stable.[73]

Silver has been separated from cobalt and nickel by cation exchange on a 1 cm x 20 cm column of Amberlite IR-120 in the Na^+ form.[74] The elution was performed with a 2 per cent solution of sodium nitrite at a flow rate of 8 ml/cm^2/min. The silver was eluted in the first 180 ml of eluant leaving the cobalt and nickel on the column. At flow rates lower than 5 ml/cm^2/min the separation was not clean.

Anion Exchange. Krause and Nelson have made a very extensive compilation of data on the adsorption of ions on Dowex-1 anion exchange resins from hydrochloric acid solutions.[75] This data indicates that silver is very strongly adsorbed at low concentrations of HCl and the adsorption decreases at higher concentrations. Silver is not adsorbed on the resin from HCl at concentrations higher than approximately 9 N.

Faris has studied the adsorption of a large number of elements on Dowex-1 in hydrofluoric acid solutions.[76] He found no adsorption of silver from HF solutions ranging in concentration from 1 M to 24 M.

The behavior of a number of metals on a 0.4 cm x 10 cm column of Dowex-2 in the chloride form has been reported.[77] Silver is eluted (in trace quantities only) with 6 to 9 N hydrochloric acid, along with Ti (IV), V (V), Pt (II), Zr, Hf, and trace quantities of tantalum. Silver may also be eluted with 1 M ammonium hydroxide, along with Pd, Sb (III), and Sb (V).

Marcus has studied the elution of silver from Dowex-1 with thiosulphate solutions.[78] Silver is very strongly adsorbed from dilute thiosulphate solutions. The distribution coefficient, D, is on the order of 10^2 to 10^3 in solutions less than 1 molar in thiosulphate. Elution from the resin may be accomplished with more concentrated thiosulphate solutions (greater than 4 molar).

The $Ag(CN)_2^-$ complex is adsorbed on Amberlite IRA-400 resin from a 0.15% sodium cyanide solution.[79] The silver may be eluted with 2 N potassium thiocyanate, with a mixture of 1 N ammonium nitrate and 0.2 N ammonium hydroxide, or with an acetone-5% HCl-5% water mixture. This system has been used to separate silver and gold from nickel, zinc, copper, iron, and cobalt.[79] The nickel and zinc are first eluted with 0.2 N HCl, and copper and iron are eluted with 2 N NaCN. The acetone-5% HCl-5% water mixture is then used to elute the silver and gold, leaving the cobalt on the column.

Strong adsorption of the $Ag(CN)_2^-$ complex has also been reported for Dowex-A-1 resin in the citrate form.[80]

8. Isotopic Exchange of Silver

Isotopic exchange is a rapid, high decontamination, single step method for separating trace quantities of radioactive silver from solutions containing other radioactive species. The exchange of silver ions between a silver chloride precipitate and a silver nitrate solution reaches isotopic equilibrium very rapidly; and because of the low solubility of silver chloride, a very favorable ratio exists at equilibrium between the silver atoms in the precipitate and those in the solution. If silver chloride is added to a solution containing only trace amounts of radioactive silver, a high percentage of this radioactive silver will have exchanged with silver in the precipitate by the time equilibrium is attained. An extensive evaluation and discussion of this procedure has been reported in Analytical Chemistry.[32]

Langer studied isotopic exchange involving silver halides ahd solutions of silver salts,[81,82] and he applied it to the determination of macro amounts of silver by a radiometric technique.[83] Pitts has presented a discussion of the theory and a mathematical treatment of the exchange of silver ions in solution with those in solid silver bromide.[84] An elemental chemical substitution of iodide for chloride in a silver chloride substrate has been employed to extract radioiodide from urine specimens.[85]

The procedure recommended for separation of silver by isotopic exchange is described below.[31,32,86] A "silver chloride electrode" of large surface area is made from a platinum gauze electrode. Silver metal is first deposited on the gauze by electrolysis for 10 minutes at 4 volts from 10 ml of a solution 3 M in sodium cyanide and 0.5 M in sodium hydroxide. The silver is rinsed with water, and then inserted in 10 ml of 0.05 M hydrochloric acid and electrolyzed as the anode for 5 minutes at 1 volt to convert the silver metal to silver chloride. The electrode is washed with 8 M nitric acid and inserted into a 1 M nitric acid solution containing the trace quantity of radioactive silver. After a sufficient contact time (with stirring), the gauze is removed, washed with 8 M nitric acid for

1 minute, and rinsed with acetone. If desired, the silver chloride may be dissolved from the gauze with a small amount of concentrated ammonium hydroxide.

The weight of silver chloride has an effect on the recovery of the silver tracer.[31,32] This effect was studied using 10-, 4-, and 1-mg amounts of silver as silver chloride on the gauze. At room temperature and with a 15-minute contact time, average yield values of 99.5 ± 0.5, 98.9 ± 0.2, and 94.5 ± 1.0 per cent, respectively, were found for seven determinations of the 10- and 4-mg, and five of the 1-mg samples. A small amount of silver chloride (on the order of 0.05 mg) is lost, apparently, through chipping or chalking of the electrode surface in the contact and washing periods. This loss is negligible in the 10-mg samples.

A 15-minute contact time under ideal conditions is more than sufficient for complete removal of the radioactive silver from solution.[31,32] Actually at 25 C, 97 per cent has been removed at the end of 5 minutes, while over 99 per cent is removed in 6 to 7 minutes. The use of a 15-minute contact period, however, assures minimization of the effects of non-ideal conditions such as small changes in acidity, stirring, and the character of the silver chloride deposit. The 1-minute nitric acid wash after exchange is necessary if high decontaminations are desired.

The temperature influences the rate of exchange. This has been studied,[87] and the results are given in Table 7. The time required for removal of 90 per cent of the silver tracer from solution is tabulated as a function of temperature. Ten mg of silver as AgCl were used in this study. As would be expected, the exchange is more rapid at high temperatures.

A study has also been made of the effects of a number of inactive chemical species which might be present in the tracer solution.[31,32] The results are given in Table 8. This study was carried out at 25 C, with 10 mg of silver as silver chloride, and with a 15-minute contact time. There are few specific interferences. The only substance showing adverse effect at low concentrations was ferric nitrate. For the other salts and acids, the effect seems to be one of total ion concentration rather than one due to any individual ion.

TABLE 7. TEMPERATURE DEPENDENCE OF Ag-AgCl EXCHANGE[87]

Temperature, C	Time for 90% Exchange, seconds
2	380
26	220
38	166
53	120
64	100
74	92
85	85
96	71

Contamination of silver separated by isotopic exchange has been tested for more than 20 representative elements.[31,32] Ten mg of silver as silver chloride, a temperature of 25 C, and a 15-minute contact time were employed. The results of this study are given in Table 9. No carriers were added to any of the tracers. Of the elements tested, only mercury and bismuth contaminated the silver gauze to an amount greater than a few parts per thousand. About 10 per cent of tracer iodide is carried on silver chloride gauze after a 15-minute contact. The 0.01 per cent figure for iodine in Table 9 was obtained after the iodine-131 solution was warmed with 0.5 ml of concentrated nitric acid and 0.5 ml of 1 <u>M</u> potassium permanganate solution to oxidize the iodide to iodate.

The silver chloride gauzes employed in most of the studies described above were prepared within one hour of use. To check the effect of aging, gauzes containing 10 mg of silver as silver chloride were stored in 8 <u>M</u> nitric acid for periods up to one week and then used for a silver separation.[31,32] Exchange yields of 99.2 ± 0.8 per cent indicated no adverse effects during one week's aging.

Silver iodide is also suitable for the exchange separation of silver.[31,32] The rate of exchange approximates that with silver chloride, as 97 per cent is removed in 6 minutes and 99 per cent in 9 minutes with 10 mg of silver as silver iodide.

TABLE 8. EFFECT OF INTERFERING SUBSTANCES ON YIELD OF SILVER IN ISOTOPIC EXCHANGE METHOD

Species	Concentration, Molar	Per Cent Yield of Ag Tracer
HNO_3	1	99
	4	99
	8	93
	12	91
	16	85
HCl	0.05	98
	0.5	99
	1.0	98
	3	89
	6	41
H_2SO_4	1.5	97
	3	90
	6	79
HF	1.1	98
	3.3	98
	6.6	83
	13.2	57
	22	18
$HC_2H_3O_2$	99%	42
$Al(NO_3)_3$	0.5	99
	1	95
	2	86
$Cu(NO_3)_2$	0.5	98
	1	97
	2	95
$Zn(NO_3)_2$	1	97
	2	95
$Fe(NO_3)_3$	0.5	95
	1	93
	2	94
$Bi(NO_3)_3$	0.5	100
	1	97
	2	93
$NaC_2H_3O_2$	0.5	96
	1	97
	2	95
C_2H_5OH	25%	98
	50%	95
	99%	36
$(CH_3)_2CO$	25%	98
	50%	95
	99%	70

9. Electrodeposition of Silver

Despite the extensive literature on the separation of silver by electrodeposition, the method has found few applications in radiochemical work. The first application of electrochemical separations to analysis of fission products was an electrodeposition of silver.[20] This procedure involved a deposition from nitric acid solution, a second deposition from a cyanide solution, dissolution of the deposit in strong nitric acid, and a final precipitation of silver chloride. Effective purification from gross fission products and silver yields of almost 100 per cent were obtained.

TABLE 9. CONTAMINATION OF SILVER BY OTHER ACTIVITIES IN ISOTOPIC EXCHANGE METHOD[32]

Radioactive Species	Per Cent Carried on Gauze[a]
Ag^{110}	99.5 ± 0.5[b]
Hg^{203} (Hg_2^{++})	7
Hg^{203} (Hg^{++})	4
Bi^{210}	1.6
Pb^{214}	<0.3
Ru^{106}, Rh^{106}	0.1
Se^{75}	0.1
Ir^{192}	0.1 - 0.01
Sn^{113}, In^{113}	0.1 - 0.01
Tl^{204} (Tl^{+})	0.04
Cr^{51}	0.01
Sb^{124}	0.01
Ta^{182}	0.01
I^{131} (IO_3^{-})	0.01-0.001
Zr^{95}, Nb^{95}	0.01-0.001
Co^{60}	0.001-0.0001
Ce^{144}, Pr^{144}	0.0001
Cs^{134}	0.0001
Sr^{90}, Y^{90}	0.0001
Ba^{140}, La^{140}	0.00005

a. Average of at least two determinations except for silver.

b. Average of seven determinations. The error is the standard deviation.

The yield data applies only to the experimental conditions described in the text.

The contamination of electrodeposited silver by a number of other activities has been studied.[31,32] The plating bath used in this study consisted of a mixture of 7 ml of 3 M sodium cyanide and 1 ml of 5 M sodium hydroxide. The silver was plated on a circular platinum gauze

TABLE 10. CONTAMINATION OF ELECTRODEPOSITED SILVER BY OTHER ACTIVITIES[31,32]

Tracer	Per Cent Carried[a]	
	Carrier Added	No Carrier Added
Ag^{110}	99 ± 1.3[b]	variable
Ce^{144}, Pr^{144}	insoluble	24
Co^{60}	insoluble	0.05
Cr^{51}	0.4	2.1
Cs^{134}	0.001	0.004
I^{131}	0.2	0.04
Ir^{192}	0.06	4 - 0.2
Ru^{106}, Rh^{106}	0.03	0.1
Sb^{124}	26	5
Se^{75}	0.04	0.05
Sn^{113}, In^{113m}	insoluble	10
Sr^{90}, Y^{90}	insoluble	2.5
Ta^{182}	insoluble	6.4
Zr^{95}, Nb^{95}	insoluble	1.0

a. Average of duplicate runs except for silver.

b. Average of quadruplicate runs. The error is the "standard deviation".

The yield data applies only to the experimental conditions described in the text.

cathode by electrolyzing at 4 volts for 15 minutes with rapid stirring. A platinum wire was used as the anode. After completion of the electrolysis, the cathode was washed with water for 1 minute and dried with acetone. The results of the study are given in Table 10. The percentage of each tracer codeposited with the silver was determined both with and without carriers except when macro amounts of the contaminants were not soluble in the plating bath.

Recovery of silver in the above procedure was quantitative when more than 2.5 mg of silver were present. With smaller amounts, the yield was reduced by dissolution of some of the silver by the plating solution during removal of the cathode.

One of the desirable features of electrodeposition lies in its usefulness in the separation of silver from halides, particularly iodine. Greiss and Rogers found that electrodeposition is also very useful for separation of traces of silver from palladium targets.[88] They studied several plating solutions and found cyanide to be the most favorable.

V. DISSOLUTION OF MATERIALS CONTAINING SILVER

Nitric acid is the reagent used most frequently in dissolving materials containing silver. Most reactor and cyclotron targets used in the production of silver isotopes are dissolved in nitric acid. These include targets of metallic palladium[60], cadmium[13], indium[13], and silver[22]. Palladium targets are only slightly soluble in concentrated nitric acid, and they are very slow to dissolve in a mixture of concentrated nitric and sulfuric acid.[53] Thus aqua regia has been employed frequently in this case.[24,53,55,59]

Many of the water-insoluble compounds of silver are soluble in nitric acid. These include the oxide, chromate, dichromate, phosphate, iodate, oxalate, cyanide, and sulfide. Some compounds are dissolved by formation of complexes of silver with complexing agents such as ammonia, cyanide, or thiosulphate. Silver chloride, oxide, chromate, dichromate, carbonate, phosphate, thiosulphate, iodate, oxalate, and cyanide may be dissolved in this manner in ammonium hydroxide. In the case of the bromide and iodide, the ammonia complex of silver is not sufficiently stable; so less dissociated complexes such as the cyanide or thiosulfate are necessary for the dissolution.

Biological and organic materials containing silver can be dissolved by ashing them in a muffle furnace and dissolving the ash in nitric acid. A wet ashing procedure in which the material is treated with nitric acid, aqua regia, or a mixture of nitric and perchloric acids may be preferred. Gorsuch has given an excellent discussion of the dissolution of organic materials containing silver.[89] He describes a wet oxidation method in which he heats a 2 g sample of cocoa with a mixture of 15 ml of nitric acid and either 10 ml of perchloric acid, 10 ml of sulfuric acid, or 10 ml of perchloric acid and 5 ml of sulfuric acid. Gorsuch also describes two dry ashing methods.[89] In one, the sample is heated until it is charred, a few drops of nitric acid is added, and heat is again applied. In the other, 5 ml of 5 N sulfuric acid or 10 ml of 7 per cent magnesium nitrate is added to the sample, the sample is dried, and it is then ashed.

A wet ashing procedure for rat tissues containing silver has been reported in which the tissue was heated to fumes with sulfuric acid and hydrogen peroxide was added dropwise until all of the organic matter was destroyed.[91] In determinations of silver in lubricating oils, the oil is ignited and burned to an ash in a platinum dish, the ignition is continued in a furnace at 500 C, concentrated nitric acid is added to the residue and evaporated to a paste, water and ammonia are added, and the mixture is boiled and filtered.[92]

VI. RADIOASSAY TECHNIQUES FOR SILVER ISOTOPES

In the radioassay of solutions or precipitates containing radioactive isotopes of silver particular attention must be paid to the decay schemes and radiations of these isotopes. Such factors as half life, type of radiation, and energy of radiation must be considered. The nuclear characteristics of the isotopes of silver can be found in the literature[92] and are summarized in Section III.

The fission product isotopes of silver are Ag^{109m}, Ag^{111}, Ag^{112}, Ag^{113}, and Ag^{114}. Silver-109m decays by an isomeric transition to stable Ag^{109}, and the 0.088 Mev gamma rays emitted in this transition may be determined with a scintillation counter. The half life of Ag^{109m} is only 40 seconds, however. Silver-111, with a half life of 7.5 days, decays by emission of 0.70, 0.80, and 1.04 Mev beta particles which may easily be assayed with a Geiger or proportional counter. Gamma rays with energies of 0.243 and 0.340 Mev are also emitted, but they are of low abundance. Silver-112 with a 3.2-hour half life and Ag^{114} with a 5-second half life both emit high energy beta radiation and gamma radiation, and they may be determined by either scintillation counting or Geiger or proportional counting. Silver-113 is a beta emitter with a 5.3-hour half life, and it is determined by assay of its 2.0 Mev beta particles.

The 0.31 Mev gamma ray emitted by Ag^{113} is of low intensity. Silver-109m, Ag^{111}, and Ag^{112} are also encountered as daughter products of Pd^{109}, Cd^{109}, Pd^{111}, Pd^{111m}, and Pd^{112}.

Silver-110m with a half life of 253 days, is one of the most frequently encountered isotopes of silver. It is produced by neutron activation and may be assayed either with a Geiger or proportional counter or with a scintillation spectrometer. Neutron activation of silver also produces 2.3-minute Ag^{108}, which may be determined by either beta or gamma assay.

The remaining isotopes of silver may be determined by both beta and gamma assay techniques except in the case of 40-day Ag^{105}, 8.3-day Ag^{106}, 44-second Ag^{107m}, 40-second Ag^{109m}, 74-second Ag^{111m}, 20-second Ag^{115m}, and 1.1-minute Ag^{117}. Silver-105 and Ag^{106} decay by electron capture and emit only X-rays and gamma rays. Silver-107m, Ag^{109m}, and Ag^{111m} decay by isomeric transition and emit only gamma rays with energies on the order of 0.09 Mev. The decay of Ag^{115m} and Ag^{117} is not well characterized, and only the emission of beta particles is known for these isotopes.

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR SILVER

PROCEDURE 1

RADIOCHEMICAL DETERMINATION OF SILVER

1. Introduction

A radiochemical procedure for the determination of silver has been developed from the yield and decontamination data presented in Tables 9 and 10 in Section IV. This procedure has been published previously by Sunderman and Meinke[1]. Isotopic exchange and electrodeposition of silver are coupled to form a procedure which may be completed in 30 minutes. Use of this procedure will give quantitative recovery of silver and decontaminate it from other activities by factors of from 10^4 to 10^{10}. All manipulations are simple, and the procedure may readily be adapted to remote operation. No precautions are required other than those normally involved in handling cyanide solutions.

2. Equipment

Battery Eliminator (Heathkit Model BE-4, Heath Co., Benton Harbor, Michigan)

Platinum Electrodes, 10 mm in diameter, 30 mm high, 52 mesh

Magnetic Stirrer

Test Tubes, 8 cm high and 15 mm in diameter.

3. Reagents

Silver plating bath: 3 M in sodium cyanide and 0.5 M in sodium hydroxide

Hydrochloric acid, 0.05 M

Nitric acid, 8 M

Silver carrier solution: $AgNO_3$, 10 mg/ml Ag^+ in water.

4. Procedure

An outline of the procedure is given in Table 1 along with the yields and decontamination factors. A more complete description of each step is given below.

Step 1. Add 10 mg of Ag^+ carrier to 9 ml of the plating bath (3 M NaCN, 0.5 M NaOH) in a 8 cm x 15 mm test tube. Connect the circular platinum gauze cathode and a platinum wire anode to a source of direct current (battery eliminator) and electrolyze at 4 volts for 10 minutes with stirring.

Step 2. Rinse the silver deposit with water, insert the electrode in 10 ml of 0.05 M hydrochloric acid, and electrolyze as the anode for 5 minutes at 1 volt to convert the silver to silver chloride.

Step 3. Wash the silver chloride with 8 M nitric acid and insert the electrode in 10 ml of the solution containing the radioactive silver tracer. Stir the solution for 15 minutes.

Step 4. Remove the electrode from the solution, wash with 8 M nitric acid for 1 minute, and rinse with water.

Step 5. Insert the electrode in 10 ml of plating solution (3 M NaCN, 0.5 M NaOH) and permit the silver chloride to dissolve.

Step 6. Remove the electrode and insert a weighed platinum gauze electrode. (If the first electrode is weighed prior to Step 1, a second electrode is not necessary.) Connect the gauze cathode and a platinum wire anode to the battery eliminator and electrolyze at 4 volts for 15 minutes with stirring.

Step 7. Remove the cathode, wash with water for 1 minute, and dry with acetone.

TABLE 1. RADIOCHEMICAL DETERMINATION OF SILVER

Ag, Ce, Co, Cr, Cs, I, Ir, Ru, Sb, Se, Sn, Sr, Ta, Zr

1. Plate 10 mg of Ag on platinum gauze.
2. Electrolyze as anode in HCl to change to AgCl.
3. Bring in contact with silver tracer solution for 15 min. at room temperature, stir during contact.
4. Wash gauze with 8 M HNO_3 for 1 min., rinse with water.

Decontamination Factors:

10^3 Ir, Ru, Se, Sn

10^4 Cr, I, Sb, Ta, Zr

10^5 Co

10^6 Ce, Cs, Sr

Isotopic Exchange with Supported AgCl Yield 100%

5. Dissolve silver chloride in 3 M NaCN-0.5 M NaOH plating solution.
6. Electrolyze at 4 volts for 15 min.
7. Wash electrode with water and acetone, and dry.

Decontamination Factors:

10^4 Sn

10^5 Ir

2×10^5 Sb, Ta

5×10^5 Cr

10^6 Ru, Zr

2×10^6 Se

4×10^6 Ce

2×10^7 I

4×10^7 Sr

2×10^8 Co

10^{10} Cs

Electrodeposition of Silver Yield 100%

8. Weigh gauze to determine yield.
9. Prepare for counting.

Step 8. Weigh the gauze to determine the yield. (The silver is deposited as the metal.)

Step 9. The gauze may be assayed in a scintillation well counter. When a more reproducible counting form is desired, the silver may be dissolved in nitric acid and precipitated as the chloride.

Reference:

1. D. N. Sunderman and W. W. Meinke, Anal. Chem. 29, 1578 (1957).

PROCEDURE 2

Source - "Determination of Silver Activity in Fission",
T. B. Novey, Paper 266 in Radiochemical Studies:
The Fission Products, edited by C. D. Coryell and
N. Sugarman, McGraw-Hill Book Co., Inc.,
New York, 1951.

A procedure for the isolation of silver from fission material is based on repeated chloride and sulfide precipitations. The determination requires about 2 hr and gives a product of more than 99 per cent radiochemical purity. The chemical yield is 60 to 90 per cent.

Discussion

The only fission-product element with an insoluble chloride is silver. A simple procedure for the isolation of silver is based on the separation of AgCl. Purification of the silver is effected by Ag_2S precipitations from an ammoniacal solution. In the procedure described here, silver is finally precipitated as AgCl for weighing and mounting.

Procedure

An irradiated uranyl nitrate sample of 5 to 50 g is dissolved in 5 to 50 ml of water, and about 20 mg of silver carrier is added. A solution of 6N HCl is added until precipitation is complete. The AgCl is centrifuged and washed, and 6N NH_4OH is added until the precipitate is dissolved. The silver is precipitated with H_2S from the cold solution.

This sulfide precipitate is centrifuged, washed, and boiled in a few milliliters of conc. HNO_3 until all the sulfur is oxidized. Silver chloride is then precipitated with HCl as before, centrifuged, and washed. The precipitations with sulfide and chloride are repeated. The chloride precipitate is filtered onto a filter-paper disk in a size 0000 Hirsch funnel, washed well with 0.1N HNO_3 and then with alcohol, and dried at 110 C. The product may be weighed to determine the chemical yield before it is mounted.

PROCEDURE 3

Source - "Improved Determination of Silver Activity in Fission", L. E. Glendenin, Paper 267 in <u>Radiochemical Studies: The Fission Products</u>, edited by C. D. Coryell and N. Sugarman, McGraw-Hill Book Co., Inc., New York, 1951.

The procedure for the determination of silver activity in fission has been improved by the addition of $Fe(OH)_3$ scavenging steps. Tracer tests and separations of silver from a fission-product mixture indicate satisfactory decontamination from other fission activities, including iodine.

1. Introduction

The separation of silver from the other fission products in a HNO_3 solution is accomplished by the precipitation of AgCl with HCl. This precipitation is specific for silver in a fission-product mixture. The purification of the silver is then effected by alternate $Fe(OH)_3$ scavengings and Ag_2S precipitations from an ammoniacal solution. The silver is finally precipitated as AgCl for weighing and mounting. The present procedure is adapted from the earlier method of Novey[1] and differs only in the addition of the $Fe(OH)_3$ scavenging steps. The decontamination from other fission activities, including iodine, is satisfactory. The chemical yield is 75 per cent or more, and the time required for a complete determination is about 1 hr. The complete procedure, together with a discussion of the developmental work, is given below.

2. Preparation and Standardization of Carrier

Dissolve 16 g of pure $AgNO_3$ in water and dilute to 1 liter. Pipet 5 ml of carrier solution into a beaker, add about 50 ml of water, and heat nearly to boiling. Add 2 ml of 6M HCl drop by drop with continuous stirring, digest the precipitate for about 1 min, and filter quantitatively with suction onto a weighed sintered-glass crucible. Wash three times with 5 ml of H_2O and three times with 5 ml of 95 per cent ethanol, rinsing down the inside of the crucible with each portion of wash liquid. Wipe the outside of the crucible dry and place in an oven at 110 C for 10 min. Cool in a desiccator and weigh as AgCl.

3. Procedure

Step 1. To the sample in a 50-ml centrifuge tube, add 2 ml of silver carrier and a few drops of Aerosol (Note 1), dilute to 20 ml, and heat nearly to boiling. Add 1 ml of 6M HCl drop by drop with stirring and digest the precipitate of AgCl for a few seconds by gentle boiling and brisk stirring (Note 2). Centrifuge, and wash the precipitate with 10 ml of H_2O.

Step 2. Dissolve the AgCl in 2 ml of 6M NH_4OH (Note 3), dilute to 10 ml, and add 5 mg of iron carrier drop by drop with stirring. Centrifuge, and discard the $Fe(OH)_3$ precipitate.

Step 3. Saturate the supernatant solution with H_2S. Centrifuge the precipitate of Ag_2S.

Step 4. Dissolve the precipitate of Ag_2S by heating with 1 ml of conc. HNO_3 (Note 4), dilute to 10 ml, neutralize with 6M NH_4OH, and add 1 to 2 ml in excess. Add 5 mg of iron carrier drop by drop with stirring. Centrifuge, and discard the precipitate.

Step 5. Repeat steps 3 and 4.

Step 6. Add 5 drops of 6M HCl and a few drops of Aerosol (Note 1); then add 2 ml of 6M HNO_3 with stirring. Heat to boiling and filter with suction onto a weighed filter-paper disk (Note 5) in a small Hirsch funnel. Wash three times with 5 ml of H_2O and three times with 5 ml of ethanol. Dry at 110 C for 10 min, weigh as AgCl, and mount.

Notes. 1. The addition of Aerosol helps to coagulate the AgCl and to prevent its adherence to the walls of the tube.

2. Digestion helps to coagulate the milky suspension of AgCl that is usually formed.

3. A little heating may be necessary.

4. A small, insoluble residue of free sulfur may be formed by oxidation of the Ag_2S. This will be removed by the $Fe(OH)_3$ scavenging precipitate.

5. The filter-paper disk is washed with ethanol and dried under the conditions of the procedure before weighing.

4. Discussion

Among the fission products the precipitation with chloride ion in acid solution is specific for silver. The most probable contaminants in the precipitation of AgCl are the halogens bromine and iodine. Precipitations of silver as Ag_2S are therefore included in the procedure for the purpose of displacing any contaminating halogen activities. To the earlier procedure of alternate precipitations of AgCl and Ag_2S developed by Novey,[1] scavenging precipitations of $Fe(OH)_3$ from an ammoniacal solution have been added to decrease general contamination. Attempts by Steinberg[2] to use a simple procedure of alternate AgCl precipitations and $Fe(OH)_3$ scavengings proved to be unsuccessful. The isolated 7.5d Ag^{111} contained a γ contamination that was not removed by this method. The contaminant was not identified, but it is probably 8.0d I^{131}, which has a γ radiation of 0.37 Mev. The addition of Ag_2S precipitations (as in the present procedure) was found by Steinberg to remove the γ contamination.

To determine the extent of iodine contamination in the silver procedure, tracer tests were made using carrier-free 8.0d I^{131} prepared by neutron irradiation of tellurium. Aliquots of the tracer solution containing 100,000 counts per minute (c/m) of 8.0d I^{131} were taken for the tests on the silver procedure. In two experiments the AgCl precipitates at the end of the complete procedure contained 8 and 10 c/m, or 0.01 per cent of the iodine tracer activity added. It is evident that for the separation of silver from the usual fission material the decontamination from iodine is quite satisfactory.

The separation of silver from general fission activities was also shown to be satisfactory by the following experiment: A fission-product concentrate was prepared from plutonium that had been irradiated in the Clinton Pile for 32 days and had stood for 42 days. The 7.5d Ag^{111} fission activity was isolated from the fission-product concentrate by a simple procedure consisting in three precipitations of AgCl with two $Fe(OH)_3$ scavengings. The isolated silver activity showed a single β component of 1.1 Mev maximum energy (by absorption in aluminum) and decayed for several half-lives with a period of 7.6 days. In the decay curve a long-lived component was finally observed which amounted to only 0.1 to 0.2 per cent of the initial activity. Since the 7.5d Ag constituted about 0.1 per cent of the total fission activity in the concentrate at the time of the silver separation, the decontamination from other fission products in this experiment was of the order of 10^6. A decontamination factor of more than 10^6 can be expected in the regular silver procedure because of the additional Ag_2S precipitations.

From the above work it is evident that the silver procedure provides sufficient purity for the usual purposes. If high purity is desired, the cycle of precipitations may be repeated as often as is necessary.

References

1. T. B. Novey, Paper 266, this volume.
2. E. P. Steinberg, private communication.

PROCEDURE 4

Source - L. J. Beaufait, Jr. and H. R. Lukens, Jr.,
"Handbook of Radiochemical Analysis, Volume II.
Radiochemical Procedures", NP-5057 (Del.),
Page 119 (1952).

1. To the solution containing the silver activity in a volume of 8 ml (in a 12-ml glass centrifuge cone), add Ag carrier. Add one drop of 1% Aerosol solution, heat to near boiling and add 1 ml of 6N HCl dropwise with stirring. Continue heating gently for one to two minutes. Centrifuge and wash the AgCl once with 5 ml of water. Discard the supernate and the wash solution.
2. Dissolve the AgCl in 1 ml of 6N NH_4OH, heating gently if necessary. Dilute the solution to 5 ml and add 5 mg of Fe^{+++} carrier dropwise with stirring. Add 2 to 3 drops of aerosol solution. Stir, centrifuge, and decant the supernate into a clean 12-ml centrifuge cone. Wash the $Fe(OH)_3$ scavenge with 2 to 3 ml of water to which a few drops of NH_4OH have been added. Combine the supernate and wash solution and discard the $Fe(OH)_3$ precipitate.
3. Add 1 drop of a 1% aerosol solution and 2 ml of 3M $(NH_4)_2S$ with stirring. Continue stirring until the Ag_2S coagulates. Centrifuge and wash once with 5 ml of water. Discard the supernate and the wash solution.
4. Dissolve the Ag_2S by adding 4 ml of HNO_3 and boiling and stirring for about 10 minutes (Note a). Place the tube in an ice-bath and carefully neutralize with NH_4OH (pH paper may be used). Add 2 ml of 6N NH_4OH and 5 mg of Fe^{+++} dropwise with stirring. Add 2 to 3 drops of a 1% aerosol solution, stir, centrifuge, and decant the supernate into a clean 12-ml centrifuge cone. Wash the $Fe(OH)_3$ scavenge with 2 to 3 ml of water to which a few drops of NH_4OH have been added. Combine the supernate and wash solution and discard the $Fe(OH)_3$ precipitate.
5. Repeat steps 3 and 4. Filter the final solution through a Whatman No. 42 filter paper in a funnel.
6. Prepare a Whatman No. 42 filter disc by washing it three times with 5-ml portions each of water and ethanol; drying at 90-100 C for ten minutes.

Cool in a desiccator for 10 minutes and weigh. Repeat this procedure until a constant weight (± 0.1 mg) has been obtained.

7. To the solution from step 5 add 2 ml of 6<u>N</u> HNO_3 and 4 drops of 6<u>N</u> HCl quickly with stirring. Filter immediately (Note b) through the prepared filter paper using the filter apparatus. Wash the AgCl three times with 5-ml portions each of water and ethanol. Dry the precipitate and disc in an oven at 90-100 C for 10 minutes, cool in a desiccator 10 minutes and weigh. Repeat the drying treatment until the weight agrees within 0.1 mg.
8. Mount and count.

NOTES

a. This treatment is necessary even if all the Ag_2S appears to dissolve immediately. A small residue of free sulfur may be formed by the oxidation of $S^=$. The sulfur will be removed by the $Fe(OH)_3$ scavenge in the following step.

b. The AgCl must be filtered before it coagulates because large particles of AgCl will give an uneven distribution of AgCl on the filter paper and thus introduce a counting error due to irregular absorption and scattering of the activity.

PROCEDURE 5

Source - R. L. Folger and H. Hicks in Report AECD-2738,
edited by W. W. Meinke, August, 1949.

Target material: 4 g U metal foil

Time for separation: 2 hr.

Type of bombardment: 184" all high energy particles

Equipment required: Centrifuge, cones, microburner, 110° oven

Yield: 80%

Degree of purification: 10^3 from all F. P. activities

Advantages: Relatively simple procedure giving good separation in high yield.

Procedure:

(1) Dissolve target in > 10 N HNO_3*. Take aliquot and dilute to ~ 5-6 N HNO_3.

(2) Add aerosol and precipitate AgCl with 1 ml 0.5 N HCl**. Wash twice with 10 ml 1 N HNO_3 containing 1 drop 2 N HCl.

(3) Dissolve AgCl in 2 ml 6 N NH_4OH, dilute to 10 ml, and add 2 mg Fe^{+3}. Centrifuge $Fe(OH)_3$ and repeat scavenge (may be done in same tube.)

(4) Saturate supernatant with H_2S in the cold, wash Ag_2S.

(5) Dissolve Ag_2S in 2 ml concentrated HNO_3, boil, dilute to approx. 4 N (8 ml) and precipitate AgCl with 1 ml 0.5 N HCl. Wash twice with HNO_3 containing 1 drop 2 N HCl.

(6) Repeat (3).

(7) Repeat (4).

(8) Dissolve Ag_2S in 1 ml concentrated HNO_3, boil to destroy or remove all H_2S dilute to 6 ml, add 1 mg Fe^{+3}, and make basic with NH_3.

(9) Add aerosol, make 2 N in HNO_3, add 2 drops 6 N HCl and boil to coagulate. Filter, wash three times with 5 ml 0.5 N HNO_3 three times with 5 ml C_2H_5OH, dry 10 min. at 110° C. Weigh as AgCl (13.28 mg per 10 mg Ag).

Remarks:

* Ag carrier should be added to the container in which target is dissolved in order to prevent loss of trace Ag by absorption in the glass. An amount of carrier should be added so that the aliquot will contain 10-20 mg.

** Boiling the solution over a microburner with stirring (being careful to avoid loss by bumping over) causes rapid and complete coagulation of AgCl.

In step 2 addition of a few drops Ba & Sr plus 2 drops 50% K_2CO_3 will provide additional decontamination from these elements.

PROCEDURE 6

Source - R. H. Goeckermann in Report AECD-2738, edited
by W. W. Meinke, August, 1949.

Target material: ~ 1 g Bi metal

Time for separation: ~ 2 hrs.

Type of bombardment: 184" all particles

Equipment required: Centrifuge, tubes, ice, 110° oven

Yield: ~80%

Degree of purification: Decontamination factor $> 10^4$ from fission and spallation products

Advantages: Good yield of pure Ag.

Procedure:

(1) To aliquot of HNO_3 solution of target add 10 mg Ag, aerosol, dilute to 20 ml, and precipitate AgCl with 1 ml 6N HCl. Wash with 10 ml H_2O.

(2) Dissolve AgCl in 2 ml 6N NH_4OH, dilute to 10 ml, and add 5 mg Fe^{+3}.

(3) Saturate supernatant with H_2S in the cold, wash Ag_2S.

(4) Dissolve Ag_2S in 1 ml concentrated HNO_3, dilute to 20 ml, and precipitate AgCl with 1 ml 6N HCl. Wash with H_2O.

(5) Repeat (2).

(6) Repeat (3).

(7) Dissolve Ag_2S in 1 ml concentrated HNO_3, dilute to 10 ml, add 5 mg Fe^{+3}, and make basic with NH_3.

(8) Add 5 drops 6N HCl to supernatant, add aerosol, make 1N in HNO_3, heat, filter, wash three times with 5 ml H_2O, three times with 5 ml C_2H_5OH, dry 10 min. at 110° C. Weigh as AgCl (13.28 mg per 10 mg Ag).

Remarks:

Wilkinson suggested an electrolysis procedure involving plating Ag^0 on the cathode from 2-3 N HNO_3 and then transferring it to the anode in a cyanide bath -- this is good unless Pt, Au, Ir, or Os are present.

PROCEDURE 7

Source - R. C. Lilly in Report AECD-2738, edited by W. W. Meinke, August, 1949.

Target material: Cd (separated isotopes)

Time for separation: 30-40 min.

Type of bombardment: Deuterons and protons - 60"

Equipment required: beakers, funnels, Hirsch funnel

Yield: ~ 90%

Degree of purification: good - at least factor of 100 from other activities present.

Advantages: Simplicity.

Procedure:

(1) Dissolve the Cd target, weighing 10-15 mg, in a few milliliters of conc. HNO_3 in a small beaker. When all of the material has dissolved, evaporate to dryness to drive off excess HNO_3.

(2) Add 3 - 4 mg In and 3-4 mg. Ag as the nitrate solutions and dilute to ~ 10 ml with H_2O.

(3) Add 1 N HCl dropwise until the Ag is completely precipitated as AgCl. Coagulate the precipitate by heating and filter through a small #42 Whatman filter paper in a short-stemmed glass funnel. (The filtrate contains the Cd and In fractions and is worked up separately as described in the procedures for Cd and In from Cd targets, Nos. 48-3 and 49-1.

(4) Wash the AgCl precipitate several times with 0.1 N HNO_3, discarding the washes. Dissolve precipitate through paper with 6 N NH_4OH, collecting the solution in another small beaker.

(5) To scavenge for In, add 2-3 mg Fe as 5 ml of $FeCl_3$ solution, stirring well during the addition. Coagulate the precipitate by heating, filter, and discard it.

(6) Re-acidify the filtrate with HNO_3 and add a few drops of 1 N HCl to make sure that the AgCl is completely precipitated. Coagulate the precipitate by heating and filter through a #42 Whatman paper disc held in a Gooch crucible or Hirsch funnel.

PROCEDURE 7 (Continued)

(7) Suck the sample as dry as possible and then pour 1-2 ml acetone through the paper to remove the residual H_2O. When the paper disc is dry, mount, under tape.

Remarks:

See Scott (Std. Meth. Chem. Anal.) for complete information on the precipitation of AgCl.

PROCEDURE 8

Source - M. Lindner in Report AECD-2738, edited by W. W. Meinke, August, 1949.

Target material: Sb (~.5 g metal)

Time for separation: 1 hr.

Type of bombardment: 184" D_2 & α

Equipment required: Lusteroid tubes, centrifuge, cones

Yield: Equal or greater than 50%

Degree of purification: At least factor of 100.

Procedure:

(1) To dissolve the Sb metal, add 15 drops of 27 <u>N</u> HF to it in a lusteroid tube in a hot water bath. Add conc. HNO_3 dropwise until dissolved (~10 min). Dilute to ~ 20 ml.

(2) To the SbF_4^- solution add 20 mg each of Te, Sn, In, Cd, Ag, Pd, Ru, Mo, & Y carriers as soluble salts. Add 2 drops conc. HCl. Centrifuge the YF_3 and AgCl precipitates.

(3) Wash the precipitate with 1 <u>N</u> HF.

(4) Dissolve out the Ag^+ from the precipitate by adding 1 ml conc. NH_4OH. Centrifuge.

(5) Dilute the supernatant to 5 ml and add 2 mg Fe^{+++} carrier. Centrifuge and discard the precipitate of $Fe(OH)_3$.

(6) Add 1 mg each Sb, Sn, In, and Cd carriers. Add 1 ml conc. HNO_3 and 1 drop conc. HCl. Centrifuge out the AgCl precipitate.

(7) Add 1 ml conc. NH_4OH to the precipitate and repeat (6).

PROCEDURE 8 (Continued)

(8) Add 2 ml 6 N NaOH to the AgCl precipitate. Digest 10 minutes in hot water bath. Dilute to 10 ml & centrifuge.

(9) Wash the Ag_2O precipitate with water and then dissolve in 1 drop conc. HNO_3.

(10) This solution can be plated or if chemical yield is to be determined the Ag should be weighed as AgCl.

PROCEDURE 9

Source - A. S. Newton in Report AECD-2738, edited by
W. W. Meinke, August, 1949.

Target material: Thorium metal (.1-1 g) Time for separation: 1 hr

Type of bombardment: 60" α's Equipment required: Standard, tank H_2S

Yield: ~ 85%

Degree of purification: ~ 10^6 except from Pd.

Procedure: Th metal dissolved in conc. HCl + a few drops .2 M solution $(NH_4)_2SiF_6$ to clear up black residue. The HCl is diluted to 2 N and an aliquot taken.

(1) Add 20 mg Ag^+ to sample after diluting to 0.3 N HCl. Digest a few min. Centrifuge AgCl precipite off and wash with 10 ml H_2O.

(2) Dissolve AgCl in 2 ml 6 N NH_4OH. Dilute to 10 ml and add 5 mg Fe^{+3}. Centrifuge off $Fe(OH)_3$. Add more Fe and recentrifuge. Saturate supernate with H_2S. Precipitate Ag_2S. Wash Ag_2S.

(3) Dissolve precipitate in 1 ml conc. HNO_3. Dilute to 10 ml. Neutralize with 6 N NH_4OH and add 1-2 ml excess. Add 5 mg Fe^{+3}. Discard precipitate.

(4) Repeat Ag_2S and $Fe(OH)_3$ precipitations.

(5) To last $Ag(NH_3)_4{}^+$ solution add 5 drops 6 N HCl, aerosol and 2 ml 6 N HNO_3. Heat and filter. Wash three times 5 ml H_2O, three times 5 ml 95% EtOH. Dry 10 min. at 110° and weigh as AgCl.

Remarks:

10 mg Ag^+ = 13.3 mg AgCl (M.W. 143.34)

This method has been described previously (Phys. Rev. 75 17 (1949)).

Ag^+ is adsorbed very rapidly by glass in carrier free solution. Dissolve and treat in quartz or lusteroid till carrier added, otherwise most of active Ag^+ may be lost.

PROCEDURE 10

Source - U. Schindewolf and M. Wahlgren, page 75 in
Report AECU-3887, edited by W. W. Meinke,
November, 1958.

Target material: Meteorite	Time for separation: 5 min.
Type of bombardment: Neutron, 5 min. 100 kw.	Equipment required: 60 mm fritted Buchner funnel, filter chimney, burner and tripod, filter flasks, aspirator, miscellaneous beakers, beaker tongs, nickel crucible, wash bottles-water, alcohol
Yield: 80%	
Advantages: rapid	

Procedure:

(1) Add 2 ml silver carrier to crucible; dry.

(2) Fuse 1 g irradiated sample with 8 g sodium peroxide for one minute. (finely ground samples)

(3) Dissolve melt in solution containing 100 ml water, 25 ml HCl.

CAUTION!!!

(4) Filter off silver chloride, wash with water.

(5) Dissolve silver chloride from fritted funnel with hot ammonium hydroxide.

(6) Add metallic zinc, swirl one minute.

(7) Pour through filter chimney.

(8) Wash final sample with hot dilute acid; dry with alcohol.

Chemical yield: thiocyanate titration.

PROCEDURE 11

Source - "Collected Radiochemical Procedures",
Los Alamos Report LA-1721, September, 1954.

This procedure is a modification of one described by L. E. Glendenin, CN-1312 (May 15, 1945).

1. Introduction

Silver is initially separated from other fission products by the specific precipitation of the chloride from nitric acid solution. The silver is then purified by ferric hydroxide scavenging and silver sulfide precipitation, both of which are performed in ammoniacal solution. After repetition of the above cycle, the silver is converted to the oxide and finally to the iodate, $AgIO_3$, in which form it is counted. The chemical yield exceeds 80%. Quadruplicate analyses may be carried out in about 3 hours.

2. Reagents

Ag carrier: 10 mg Ag/ml (added as $AgNO_3$ in very dilute HNO_3)--standardized

Fe carrier: 10 mg Fe/ml (added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl)

HCl: 1$\underline{M}$

HCl: 6$\underline{M}$

HNO_3: 6$\underline{M}$

HNO_3: conc.

H_2SO_4: conc.

HIO_3: 2$\underline{M}$

NaOH: 6$\underline{M}$

NH_4OH: conc.

$(NH_4)_2S$: saturated solution

Aerosol: 0.1% in H_2O

Ethanol: 95%.

3. Equipment

Bunsen burner

Drying oven

Centrifuge

Block for holding centrifuge tubes

Mounting plates

Forceps

Pipets: assorted sizes

Wash bottle

Ground-off Hirsch funnels: Coors 000A (one per sample)

Filter chimneys (one per sample)

Filter flasks

60-ml sintered glass crucibles: medium porosity (one per standardization)

No. 42 Whatman filter circles: 7/8" diameter--weighed

40-ml conical centrifuge tubes: Pyrex 8320 (five per sample; one per standardization)

Stirring rods.

4. Preparation and Standardization of Carrier

Dissolve 15.75 g of $AgNO_3$ in a minimum amount of H_2O, add a few drops of HNO_3, and dilute the solution to 1 liter.

Pipet exactly 5 ml of the carrier solution into a 40-ml conical centrifuge tube and dilute to 20 ml with H_2O. Add 1 ml of 2M HIO_3 and stir to coagulate the precipitate which forms. Add an additional drop of HIO_3 to test for completeness of precipitation. Filter the precipitate into a weighed 60-ml sintered glass crucible of medium porosity. Wash the precipitate with 5 ml of 95% ethanol and dry in an oven at 110° for 15 min. Cool and weigh as $AgIO_3$.

Four standardizations, with results agreeing within 0.5%, are performed.

5. Procedure

Step 1. To the sample in a 40-ml conical centrifuge tube, add exactly 2 ml of Ag carrier and dilute the solution to 20 ml with 6M HNO_3. Add 1 ml of aerosol solution and heat to boiling. Precipitate AgCl by the addition of 1 ml of 1M HCl. Heat until the AgCl has coagulated. Centrifuge and discard the supernate.

Step 2. Dissolve the AgCl in 2 ml of conc. NH_4OH. Dilute to 20 ml with H_2O and add 1 ml of Fe carrier. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate.

Step 3. To the solution add 1 ml of saturated $(NH_4)_2S$ solution. Stir vigorously and centrifuge (Note 1). Discard the supernate.

Step 4. Dissolve the Ag_2S precipitate by heating with 1 ml of conc. HNO_3. Dilute to 20 ml with H_2O and precipitate AgCl by the addition of 1 ml of 1M HCl as in Step 1.

Step 5. Repeat Steps 2 and 3.

Step 6. Dissolve the Ag_2S precipitate by heating with 1 ml of conc. HNO_3. Make the solution alkaline with 6M NaOH, and then add 3 drops in excess. Centrifuge the Ag_2O precipitate, and discard the supernate. Dissolve the Ag_2O in 4 drops of conc. H_2SO_4 and evaporate to dryness. Cool.

Step 7. Dissolve the residue in 20 ml of distilled H_2O and add 1 ml of 2M HIO_3. Centrifuge and discard the supernate.

Step 8. Dissolve the $AgIO_3$ precipitate in 4 drops of conc. NH_4OH. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, centrifuge and discard any S residue.

Step 9. Add 3 drops of conc. H_2SO_4 to the solution and filter the $AgIO_3$ precipitate on a weighed No. 42 Whatman 7/8" filter circle, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with 5 ml of 95% ethanol. Dry for 15 min at 110°. Cool, weigh, and mount (Note 2).

Notes

1. Although the precipitation of AgCl in acid solution is specific for Ag among the cations in fission products, it is possible that the precipitate may be contaminated with bromine and iodine. Therefore, the Ag_2S precipitations are carried out to displace any contaminating halogen activities.

2. Beta-counting for 7.5d Ag^{111} activity is begun about 16 hours after completion of the chemistry to permit 3.2h Ag^{112} to decay sufficiently so as not to interfere.

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