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The Radiochemistry of Fluorine, Chlorine, Bromine and Iodine

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January 1960

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, the problems of stockpiling uncontaminated materials, the 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

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The Radiochemistry of Fluorine, Chlorine, Bromine and Iodine

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January 1960

I. GENERAL REFERENCES TO THE INORGANIC AND ANALYTICAL CHEMISTRY OF THE HALOGENS

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II. TABLE OF ISOTOPES* OF FLUORINE, CHLORINE, BROMINE AND IODINE

Isotope	Half Life	Type of Decay	Method of Preparation
F^{17}	~ 70 sec	β^+	$N^{14}(\alpha,n)$ $O^{16}(d,n)$ $O^{16}(p,\gamma)$ $F^{19}(\gamma,2n)$
F^{18}	~ 110 min	β^+ 97% EC 3%	$O^{16}(\alpha,pn)$ $O^{18}(p,n)$ $F^{19}(n,2n)$ $F^{19}(\gamma,n)$ $Ne^{20}(d,\alpha)$ and others
F^{19}	stable (abundance 100%)		Natural
F^{20}	10.7 sec	β^-	$F^{19}(d,p)$ $F^{19}(n,\gamma)$ $Na^{23}(n,\alpha)$
Cl^{32}	~ 0.3 sec	β^+ $\alpha \sim 10^{-2}\%$	$S^{32}(p,n)$
Cl^{33}	~ 2.4 sec	β^+	$S^{32}(d,n)$ $S^{33}(p,n)$ $Cl^{35}(\gamma,2n)$
Cl^{34m}	32.4 min	β^+ ~ 50% IT ~ 50%	$Cl^{35}(p,pn)$
Cl^{34}	~ 1.5 sec	β^+	Daughter Cl^{34m} $P^{32}(\alpha,n)$ $S^{33}(d,n)$ and others
Cl^{35}	stable (abundance ~ 75.5%)		Natural
Cl^{36}	4.4×10^5 year	β^- 98.3% EC(K) 1.7%	$Cl^{35}(n,\gamma)$ $Cl^{35}(d,p)$
Cl^{37}	stable (abundance ~ 24.5%)		Natural
Cl^{38}	~ 37 min	β^-	$Cl^{37}(d,p)$ $Cl^{37}(n,\gamma)$ and others

II. TABLE OF ISOTOPES* OF FLUORINE, CHLORINE, BROMINE AND IODINE (Cont'd)

Isotope	Half Life	Type of Decay	Method of Preparation
Cl^{39}	~ 1 hr	β^-	$A^{40}(\gamma,p)$ Spall Fe, Co, Cu, As
Cl^{40}	1.4 min	β^-	$A^{40}(n,p)$
Br^{74}	~ 40 min	β^+ EC	$Cu^{65}(C^{12},3n)$
Br^{75}	~ 1.6 hr	β^+ EC	$Cu^{65}(C^{12},2n)$ $Se^{74}(d,n)$ $Se^{74}(p,\gamma)$
Br^{76}	~ 17 hr	β^+	$As^{75}(\alpha,3n)$ $Se^{76}(p,n)$
Br^{77}	~ 57 hr	EC 99%; β^+ 1% EC 95%; β^+ 5%	$As^{75}(\alpha,2n)$ $Se^{74}(\alpha,p)$ $Se^{76}(d,n)$
Br^{78m}	6.4 min	IT	$As^{75}(\alpha,n)$ $Se^{77}(d,n)$ $Se^{78}(p,n)$ $Br^{79}(\gamma,n)$ $Br^{79}(n,2n)$
Br^{78}	< 6 min	β^+	Daughter Br^{78m}
Br^{79}	stable	(abundance ~ 50.5%)	Natural
Br^{80m}	~ 4.5 hr	IT	$Se^{80}(d,2n)$ $Se^{77}(\alpha,p)$ $Se^{80}(p,n)$ $Br^{79}(n,\gamma)$ and others
Br^{80}	~ 18 min	β^- 92% β^+ ~3% EC ~5%	$Se^{80}(p,n)$ $Br^{79}(n,\gamma)$ $Br^{79}(d,p)$ $Br^{81}(\gamma,n)$ Daughter Br^{80m} $Br^{81}(n,2n)$
Br^{81}	stable	(abundance ~ 49.5%)	Natural

II. TABLE OF ISOTOPES* OF FLUORINE, CHLORINE, BROMINE AND IODINE (Cont'd)

Isotope	Half Life	Type of Decay	Method of Preparation
Br^{82}	~ 36 hr	β^-	$Se^{82}(p,n)$ $Se^{82}(d,2n)$ $Br^{81}(n,\gamma)$ and others
Br^{83}	~ 2.4 hr	β^-	$Se^{82}(d,n)$ $Rb^{87}(\gamma,\alpha)$ Spall-fission Ta, Hg, Pb, Bi, Th Fission Th, U^{233}, U, Pu Daughter Se^{83}
Br^{84}	~ 32 min	β^-	$Rb^{87}(n,\alpha)$ Spall-fission Bi, U Fission Th, U Daughter Se^{84}
Br^{85}	3.0 min	β^-	Fission U
Br^{87}	~ 55 sec	β^- β^-n(~ 2%)	Fission U
Br^{88}	15.5 sec	β^-	Fission U
I^{119}	~ 19 min	β^+	$Pd^{110}(N^{14},5n)$ or $Pd^{108}(N^{14},3n)$ Spall Cs
I^{121}	~ 2 hr	β^+	$Sb^{121}(\alpha,4n)$ Spall Cs
I^{122}	~ 4 min	β^+	$Sb^{121}(\alpha,3n)$ $Te^{122}(p,n)$ Daughter Xe^{122}
I^{123}	13.0 hr	EC	$Sb^{121}(\alpha,2n)$ Daughter Xe^{123}
I^{124}	~ 4 day	EC ~ 70% β^+ ~ 30%	$Sb^{121}(\alpha,n)$ $Sb^{123}(\alpha,3n)$ $Te^{124}(p,n)$ and others

II. TABLE OF ISOTOPES* OF FLUORINE, CHLORINE, BROMINE AND IODINE (Cont'd)

Isotope	Half Life	Type of Decay	Method of Preparation
I^{125}	~ 60 day	EC	$Sb^{123}(\alpha,2n)$ $Te^{124}(d,n)$ Spall-fission Bi Daughter Xe^{125}
I^{126}	~ 13 day	EC 55% β^- 44% β^+ ~1%	$Sb^{123}(\alpha,n)$ $Te^{125}(d,n)$ $Te^{126}(p,n)$ $I^{127}(n,2n)$ and others
I^{127}	stable (abundance 100%)		Natural
I^{128}	~ 25 min	EC ~ 6% β^- ~ 94%	$I^{127}(n,\gamma)$ $Te^{128}(d,2n)$ $Te^{128}(p,n)$
I^{129}	1.7 x 10^7 year	β^-	Fission U
I^{130}	~ 12.5 hr	β^-	$Te^{130}(d,2n)$ $Te^{130}(p,n)$ $I^{129}(n,\gamma)$ $Cs^{133}(n,\alpha)$
I^{131}	~ 8.1 day	β^-	$Te^{130}(d,n)$ Spall-fission Th, U Fission Th, U, U^{235}, Pu Daughter Te^{131}
I^{132}	~ 2.3 hr	β^-	Spall-fission U Fission Th, U, U^{233} Daughter Te^{132}
I^{133}	~ 21 hr	β^-	Spall-fission Pb, U Fission U, Pu Daughter Te^{133}
I^{134}	~ 52.5 hr	β^-	Spall-fission U Fission Th, U, U^{235}, Pu Daughter Te^{134}

II. TABLE OF ISOTOPES* OF FLUORINE, CHLORINE, BROMINE AND IODINE (Cont'd)

Isotope	Half Life	Type of Decay	Method of Preparation
I^{135}	~ 6.7 hr	β^-	Spall-fission U Fission Th, U, Pu Daughter Te^{135}
I^{137}	~ 22 sec	$\begin{cases}\beta^- \\ \beta^- n(\sim 6\%)\end{cases}$	Fission U, Pu
I^{138}	5.9 sec	β^-	Fission U, ancestor Cs^{138}
I^{139}	2.7 sec	β^-	Fission U, ancestor Ba^{139}

*Only those isotopes are listed which fall in categories A and B in "Table of Isotopes", D. Strominger, J. M. Hollander and G. T. Seaborg, Reviews of Modern Physics, 30, No. 2, Part II, April 1958.

III. A REVIEW OF SOME ASPECTS OF HALOGEN CHEMISTRY OF INTEREST TO RADIOCHEMISTS

1. General Properties of the Halogens

Fluorine, chlorine, bromine, and iodine, with the respective atomic numbers 9, 17, 35 and 53, along with astatine, comprise the halogens. These elements possess an s^2p^5 valence shell configuration. Fluorine differs markedly in its chemistry from the other halogens. The difference observed are largely attributable to its very high electronegativity, small size, and inability to accommodate more than eight electrons in the valence shell.

The halogens exhibit a marked tendency to attain inert gas configurations, i.e., an s^2p^6 outer shell configuration. This is manifested in the diatomic nature of the elementary molecules, in the relatively large amounts of energy required to dissociate these molecules (heat of dissociation, kcal/mole: F_2, 38 ± 3; Cl_2, 57.2; Br_2, 45.4; I_2, 35.5), and in the large values for the electron affinities of the atoms (F, 83 ± 3; Cl, 86.5; Br, 81.5; I, 74.2 kcal/g atom).

The great tendency for the halogens to reach octet configurations is reflected in the abundance of halide salts and in the large number of compounds in which the elements show a covalence of one. For fluorine, this is the only covalence permitted; for the other halogens, where the valence shell can hold more than eight electrons, covalences greater than one are not uncommon. Examples in which chlorine, bromine, and iodine have more than eight electrons in the valence shell are to be found among the interhalogens, where such compounds as ClF_3, BrF_5, and IF_7 have been characterized. Thus in chlorine trifluoride there are ten electrons around the central chlorine atom, three pairs shared with fluorine atoms and two unshared pairs. As would be expected, iodine, the largest of the halogens, can form the greatest number of covalent bonds.

In their compounds with metals the halogens are necessarily in a negative one oxidation state. With active metals which give rise to large cations of low charge, i.e., sodium, calcium, this oxidation state is an ionic one. On the other hand, with metals, even active ones such as beryllium and aluminum, which are potential sources of ions of relatively high charge density, the bonds between halogen, particularly chlorine, bromine or iodine, and metal are frequently covalent in character. With a metal exhibiting a variety of oxidation states, the covalent character of any one halide type increases with increasing oxidation state of the metal. This trend is generally accompanied by increasing volatility as well as increasing solubility in non-polar organic solvents (e.g., compare $FeCl_2$ and $FeCl_3$).

In union with other non-metals, fluorine, the most electronegative element known, invariably may be regarded as being in a negative oxidation state. The other halogens may be considered as exhibiting either electronegative or electropositive character depending upon the electronegativity of the element to which they are joined. The most common situations in which chlorine, bromine, and iodine exhibit positive oxidation states are to be found in the interhalogens and in the various oxyhalogen compounds. Positive oxidation states of 1, 3, 5, and 7 are known. It should be emphasized that in these positive oxidation states the halogens are joined to the more electronegative element by essentially covalent bonds.

It is noteworthy that iodine, the least electronegative halogen, is actually capable of forming the cationic species I^+. This extremely unstable entity can be considerably stablized by coordination with such organic bases as pyridine. Thus such compounds as $[I\ py_2]NO_3$ and $[I\ py_2]ClO_4$, among others, have been prepared.

Inasmuch as changes in oxidation state are frequently of significance in radiochemical procedures for the analysis of chlorine, bromine and iodine, the potential relationships which exist among the various oxidation states of these elements are shown on page 8.

Acidic Solutions:

$$\begin{tikzcd}
Cl^- \arrow[r, "-1.36"] & Cl_2 \arrow[r, "-1.62"] \arrow[rrr, bend right, "-1.47"'] & HClO \arrow[r, "-1.63"] & HClO_2 \arrow[r, "-1.21"] & ClO_3^- \arrow[r, "-1.19"] & ClO_4^-
\end{tikzcd}$$

$$\begin{tikzcd}
Br^- \arrow[r, "-1.07"] & Br_2 \arrow[r, "-1.59"] \arrow[rr, bend right, "-1.52"'] & HBrO \arrow[r, "-1.49"] & BrO_3^-
\end{tikzcd}$$

$$\begin{tikzcd}
I^- \arrow[r, "-0.53"] & I_2 \arrow[r, "-1.45"] \arrow[rr, bend right, "-1.20"'] & HIO \arrow[r, "-1.14"] & IO_3^- \arrow[r, "ca.-1.70"] & H_5IO_6
\end{tikzcd}$$

Basic Solutions:

$$\begin{tikzcd}
Cl^- \arrow[r, "-1.36"] \arrow[rr, bend right, "-0.88"'] & Cl_2 \arrow[r, "-0.40"] & ClO^- \arrow[r, "-0.65"] & ClO_2^- \arrow[r, "-0.35"] & ClO_3^- \arrow[r, "-0.36"] & ClO_4
\end{tikzcd}$$

$$\begin{tikzcd}
Br^- \arrow[r, "-1.07"] \arrow[rr, bend right, "-0.49"'] & Br_2 \arrow[r, "-0.45"] & BrO^- \arrow[r, "-0.54"] & BrO_3^-
\end{tikzcd}$$

$$\begin{tikzcd}
I^- \arrow[r, "-0.53"] \arrow[rr, bend right, "-0.49"'] & I_2 \arrow[r, "-0.45"] & IO^- \arrow[r, "-0.14"] & IO_3^- \arrow[r, "ca.\ -0.7"] & H_3IO_6
\end{tikzcd}$$

2. Observations on Species of Significance in the Analytical Chemistry of Halogens

In view of the fact that the formation of elementary bromine and iodine is of importance in a number of methods for the analytical determination of these elements, some properties of these substances are described. As is evident from the potential data cited above, both bromine and iodine are fairly strong oxidizing agents. Bromine is rather soluble in water, 3.55 g dissolving in 100 g of water at 20°; the solubility of iodine is much smaller (0.34 g per liter of solution at 25°). For both elements, solution in water is accompanied by the main reaction

$$X_2 + H_2O = H^+ + X^- + HXO.$$

For bromine, the equilibrium constant for this reaction is 5×10^{-9}; for iodine, 3×10^{-13}. (For chlorine, the constant is 4×10^{-4}. The reaction is of no significance for fluorine, which vigorously liberates oxygen and ozone from liquid water with the formation of hydrofluoric acid.) In cold dilute alkaline solutions hypohalite salts are formed; in warm concentrated alkaline solutions the hypohalite ion disproportionates to halate (XO_3^-) and halide ions.

Bromine is completely miscible with common organic solvents. Iodine is generally appreciably soluble in organic solvents. In solvents exhibiting no donor characteristics, e.g., carbon disulfide, chloroform, carbon tetrachloride, the solutions are violet in color. In aromatic solvents such as benzene and toluene the solutions are red. In solvents which may be regarded as typical Lewis bases (e.g., ether, pyridine), iodine is most soluble and gives brown solutions. There is little doubt that in both the red and brown solutions solvation of the iodine occurs.

An important characteristic of elementary iodine is its ability to combine with iodide ion to form polyiodide anions, I_n^-, of which the triiodide ion, I_3^-, is the most stable. Other polyiodide ions which have been identified are I_5^-, I_7^- and I_9^-. The most stable polyiodide salts are formed with large cations, e.g., Cs^+, quaternary ammonium ions. Tribromides are known, but they are much less stable than triiodides. The existence of the trichloride ion in solution has been definitely established, but no stable solid salts of this anion have been isolated. The trifluoride ion is unknown. The trend in stability of the trihalide ions in aqueous solution is shown by the values for the equilibrium constants for the reaction.

$$X_2 + X^- = X_3^-$$

For iodine the constant at 25° is 725; for bromine 17.8; and for chlorine 10^{-2}.

Most of the analytical determinations for the halogens involve precipitation reactions of the halide ions. Fluorine may be precipitated as the calcium salt (K_{sp} 18°: 3.4×10^{-11}) or as lead chlorofluoride $PbF_2 \cdot PbCl_2$). Precipitation of the calcium salt is not entirely satisfactory even when the solution to be tested contains appreciable amounts of fluoride, low results commonly being obtained. Precipitation of lead chlorofluoride is usually carried out in the pH range 3.6 - 5.6; the precipitate can be weighed as such, or the fluroine content can be determined indirectly from titration of the chloride.

Chloride, bromide, or iodide can be determined by precipitation with silver ion (K_{sp} 25°: AgCl 1.56×10^{-10} ; AgBr 7.7×10^{-13}; AgI 1.5×10^{-16}. Silver fluoride exhibits a solubility of 181.5 g per 100 g of water at about 20°.) The analytical procedure may be a gravimetric one or a titration. Iodide may be precipitated and determined as the palladium(II) salt. As a matter of fact, precipitation by means of palladium(II) chloride from a slightly acidic solution is a satisfactory method for the separation of iodide from chloride and bromide. A more common way of separating iodide from solution with the other halides is by the addition of nitrous acid, which converts iodide to free iodine and is without effect on the remaining halides. Separation of bromide from chloride can be accomplished by oxidation of the former to elementary bromine by potassium permanganate in acetic acid solution. It can also be affected from the silver salts; silver bromide is essentially insoluble in an aqueous solution of ammonium carbonate, whereas the chloride is soluble.

3. Ion Exchange Separations

Ion exchange has been used infrequently for separation of the halogens from each other, probably because the well known conversion to the free element followed by extraction into an organic solvent is so well established.

An ion exchange separation of the halide ions was demonstrated early in the history of modern exchange materials.[1] The ammonium salts of fluoride, chloride, bromide, and iodide were absorbed on Dowex-2 (100-200 mesh) in the nitrate form. Elution was performed at room temperature with 1M sodium nitrate at a pH of 10.4. Fluoride comes off first. Peak to valley ratios of 100 to 600 between F^-, Cl^-, Br^-, and I^- were obtained indicating good separation.

A similar separation has been used for determining Cl and Br in mixtures of the two by absorption[2] on a strong base anion resin, XE 67 supplied by Rohm and Haas Company. The eluting agent was 0.6M $NaNO_3$ containing a nonionic wetting agent. A further application of this method has been used for the analytical separation of Cl, Br, and I on Dowex 1-X10 resin,[3] the eluting agent was 0.5$\underline{M}$ $NaNO_3$. Another halide separation on a strong base resin used 0.5$\underline{M}$ $NaNO_3$ to elute Cl^-. The eluant concentration was then increased to 2$\underline{M}$ to accelerate the elution of Br^- and I^-.[4]

A method for separating Cl^-, Br^- and I^- makes use of precipitation chromatography.[5] A column is made of $AgNO_3$ or Ag_2SO_4 and alumina in a 1 to 9 ratio of precipitant to filler. The mixture of ions is passed through the columns and developed in sunlight for 5 to 15 minutes. The limit of identification is 8 γ for I^- and 14 to 15 γ for Br^- and Cl^-.

The halides have been separated on paper impregnated with Ag_2CrO_4.[6] Paper chromatography and activation analysis have been combined for the determination of S, Br, and Cl in organic compounds.[7]

Fluoride has been quantitatively separated from 500 times as much phosphorus on a Dowex 1-X10 column in the hydroxide form.[8] The 100-200 mesh, strong base resin was cycled three times with 3$\underline{N}$ NaOH and 3$\underline{N}$ HCl, then left in the hydroxide form. The elution was performed with 0.5$\underline{N}$ NaOH.

Fluoride has been separated from aluminum by eluting from the alkaline form of a strong base resin.[9] The aluminum comes off the column first.

Rates of uptake and an affinity series for several anions including the halides have been determined for hydrous zirconium oxide.[10] The affinity series determined with 0.1$\underline{N}$ solutions is: Cl^-, $NO_3^- > Br^-$, I^-, $CrO_4^= \gg SO_4^=$.

A synthetic inorganic ion exchanger was used to remove large quantities of unwanted F^{18} activity that formed as a by-product in a cyclotron irradiation.[11] The solution in concentrated HCl was passed through an Al_2O_3 column and more than 90% of the fluoride was absorbed.

4. Solvent Extraction Separations

Extraction of the free element form of the halogen into an organic solvent (CCl_4,$CHCl_3$) after use of the proper oxidizing agent has long been a favored separation method for Cl, Br, and I. Several detailed examples are given in the section on procedures.

Because many organic compounds of the halogens can be prepared, Szilard-Chalmers extraction systems have been very commonly used to increase the specific activity of a halogen.[12] The recoil energy of the incident nuclear particle breaks the bond between the halogen and the carbon atom. Extraction of the organic solution with water then yields a high specific activity of the halide.

Neutron activation followed by extraction of Br and I and the distillation of Cl has been used as an analytical method to determine trace amounts of mixed halides.[13]

Tetraphenyl stibonium sulfate has been used to extract fluoride from a solution in 97-98% yield.[14] The method is more useful for concentration purposes than as a highly specific separation. A few drops of H_2SO_4 are added to the solution containing up to 5 mg of F^-. 0.125 millimole of tetraphenyl stibonium sulfate is added and the volume brought to 19 ml. It is shaken with three successive 5 ml portions of CCl_4 and the organic layer is evaporated and weighed.

5. Distillation Separations

Distillation of fluorine as hydrofluosilicic acid is commonly used for separating fluoride from interfering ions before a titration or precipitation.[15,16,17]

Chlorine, bromine, and iodine can be separated by selective oxidation and distillation of the element. Iodine is oxidized by addition of $NaNO_2$ in dilute H_2SO_4.[18] Bromine can be oxidized with telluric acid,[19] $KMnO_4$ in acetic acid, or $KH(IO_3)_2$ in dilute nitric acid. Chlorine can be oxidized by addition of concentrated HNO_3.

6. Exchange Reactions

A prime requisite in radiochemical analytical procedures is the complete exchange between the radioactive species being determined and carrier. Observations on exchange between various halogen entities in aqueous medium are summarized below.

Exchange between free halogen and halide ion in solution is complete within the minimum time of mixing and separation. Three plausible mechanisms for exchange have been postulated.[20] These involve the equilibria shown below:

(1) $X_2 + X^{*-} = X_3^{*-}$ (X = Cl, Br, I) $K_1 = 10^{-2}$

(2) $X_2 + OH^- = HXO + X^-$ $K_2 = 4 \times 10^{10}$

(3) $X_2 + H_2O = HXO + H^+ + X^-$ $K_3 = 4 \times 10^{-4}$

In view of the high exchange velocity it is extremely difficult to distinguish between these three mechanisms. However, there is strong evidence[21] that exchange occurs by mechanism (1), that is, through trihalide ion formation.

Tracer aqueous bromine exchanges rapidly with freshly precipitated silver bromide.[22]

Exchange between elementary chlorine and chlorate ion in acidic solution both at room temperature and elevated temperatures is extremely slow.[23] Neither elementary chlorine nor chloride ion exchange with perchloric ion either in alkaline or acidic solution.[24] Exchange of chlorine activity between hypochlorite and chlorite ions in basic solution is very slow.[23] Exchange between chlorate ion and perchlorate ion does not occur at room temperature, or even at 90°, in neutral, basic or acidic solution.[25]

The rate of exchange between freshly formed silver bromide and aqueous bromide ion is very rapid, homogeneous distribution of activity being attained within a few seconds.[26] It has been reported[27] that the rate of exchange between bromine and bromate ion in acidic aqueous solution is given by the expression

$$R = k[Br_2]^m[BrO_3^-]^n[H^+]^p$$

where $k = 0.023$ mole$^{-2.1}$l.$^{2.1}$hr^{-1}, $m = 0.3 \pm 0.05$, $n = 1.7 \pm 0.05$, and $p = 1.1 \pm 0.05$. It is proposed that the following set of reactions is applicable to the system:

$$HBr + HBrO_3 = HBrO_2 + HBrO$$

$$HBr + HBrO_2 = 2\ HBrO$$

$$HBrO + HBr = Br_2 + H_2O$$

In the radiochemical determination of bromine activities in fission products, rapid exchange can be ensured by the addition of bromate carrier to the sample and its reduction to bromide ion.[28]

The exchange in acidic solution of elementary iodine with iodate or periodate (IO_4^-) ion, and of iodate with periodate in acidic or alkaline solution is slow.[29,30] The experimentally observed[31] rate law for the iodine-iodate exchange reaction has been determined to be

$$R = (I_2)^{0.6}(H^+)^{1.8}(IO_3^-)^{0.8}[k(IO_3^-) + k'(X^-)]\Gamma$$

in which X^- may be perchlorate, nitrate or sulfate ion, and Γ is the appropriate function of the activity coefficients of the reactants and transition states. At 25°, k has the value 7.40 ± 0.25 l.$^{3.2}$ mole$^{-3.2}$ hr^{-1} and k' is approximately 0.15 l.$^{3.2}$ mole$^{-3.2}$ hr^{-1} for $X^- = ClO_4^-$. The activation energy is about 20 kcal. mole^{-1}. The exchange reaction has been shown to occur by the same mechanism as the iodide-iodate reaction; the rate law for the latter reaction at low iodide ion concentration is given by the expression

$$-d(IO_3^-)/dt = (I^-)(IO_3^-)(H^+)^3[k_6(IO_3^-) + k_6'(X^-)]\Gamma$$

where at 25° k_6 is $(5.7 \pm 1.3) \times 10^6$ l.^{5} mole^{-5} sec^{-1}, and k_6' for $X^- =$

ClO_4^- is about 1.1×10^5 l.^{5} mole^{-5} sec^{-1}. Studies[32] of the iodine-iodate exchange reaction in solutions of constant ionic strength and having high $(ClO_4^-)/(IO_3^-)$ ratios give the following rate law:

$$R = k(I^-)(IO_3^-)(H^+)^3$$

This is entirely consistent with the previous rate expression noted immediately above.

In radiochemical analyses for iodine, complete exchange of radioiodine with carrier presumably can be obtained by the addition of the latter as iodide ion and subsequent oxidation to periodate, e.g., by hypochlorite ion in basic solution, followed by reduction to iodide by means of bisulfite in acidic solution.[33]

IV. COLLECTION OF RADIOCHEMICAL PROCEDURES FOR FLUORINE, CHLORINE, BROMINE, AND IODINE

PROCEDURE I - FLUORINE

Source - A. Turkevich, unpublished Los Alamos work in 1955

Experimental work on a radiochemical procedure for fluorine which would provide a very high decontamination factor from fission products, notably bromine and iodine, was begun by Turkevich in 1955. The procedure was not completely developed but is presented here as a starting point for a modified procedure.

1. The sample was contained on 2 gms of organic fiber filter paper. It was brought into a soluble form by fusion in a Pt crucible with 22 gms of anhydrous K_2CO_3 to which 5 ml of carrier had been added (2.642 gms $KF \cdot 2\ H_2O$ in 100 ml of H_2O). The covered Pt crucible was gradually inserted into a 500°C oven. After 30 min at 500°C, the mass was charred black. It was then placed in an oven at 850°C and the carbonate was completely fused for several minutes. The cooled melt was dissolved in hot water.

2. The water solution was neutralized in the presence of bromphenol blue with 6N HNO_3. The solution must not be permitted to become acidic but should remain slightly basic.

The pH was then adjusted with NaOH to a faint blue indicator color, then 2 ml of 6N HCl, 5 gm of $Pb(NO_3)_2$ in solution, and 5 gm of sodium acetate in solution were added; the mixture then was stirred and digested for one-half hour to precipitate PbClF.

3. The precipitate of PbClF was dissolved in 20 ml hot water containing a few drops of conc HNO_3. $AgNO_3$ was then added in slight excess.

The precipitate of AgCl was centrifuged off and to the supernate a slight excess of HCl was added to precipitate excess silver. The AgCl was again centrifuged off.

4. The solution was again neutralized with NaOH to a faint blue color of bromphenol blue indicator, and 2 ml of 6<u>N</u> HCl, 5 gm of $Pb(NO_3)_2$ and 5 gm of sodium acetate were added. The precipitate was digested, centrifuged, and washed with cold water.

4. The PbClF precipitate was dissolved in hot water containing a few drops of HNO_3. It was transferred to a distillation flask with one gm of crushed Pyrex glass. 30 ml of 70% $HClO_4$ was added. Steam was passed in and the flask temperature held at 135°-150°C. A 50 ml of distillate was collected in 45 min in a flask containing, initially, 30 ml of water plus a dozen NaOH pellets.

5. The distillate was neutralized with HNO_3, excess La^{+3} added, and LaF_3 precipitated. The yield from the above procedure was very small and was not determined. (Note 1).

Notes

1. It was suggested that the first step after fusion should be the distillation of H_2SiF_6. This should then be followed by PbClF and AgCl scavenging steps and a second distillation of H_2SiF_6. Finally the fluorine should be precipitated as PbClF, in which form it would be weighed and counted.

PROCEDURE 2 - CHLORINE

Source - W. W. Meinke, report AECD-2738, pp. 22. Aug. 1949

Element separated: Chlorine	Degree of purification: 10^3
Target material: Copper	Procedure by: Batzel
Type of bbdt: All -	Time for sep'n: 30 minutes
Yield: 60%	Equipment required: standard

Procedure:

(1) Dissolve the copper in concentrated HNO_3 containing 5 mg of chlorine carrier (1-2 ml concentrated HNO_3 for 0.1-0.3 grams copper foil).

(2) Distill the chlorine into a centrifuge tube containing 2 cc of water, 2-3 drops of concentrated HNO_3, and sufficient $AgNO_3$ to precipitate the chlorine as AgCl.

(3) Heat almost to boiling, centrifuge the precipitate and wash with 3 cc of 2N HNO_3.

(4) Dissolve the AgCl in 3 cc of 5 N NH_4OH and add a drop of hold-back carriers from standard 10 mg/ml solns, for Cu, Ni, Co, Zn, Fe (add as nitrates or sulfates) and then add 2 drops of 0.5 N KI.

(5) Centrifuge and wash the precipitate with 2 cc of 5 N NH_4OH. Add the wash to the supernate and add excess $AgNO_3$ to precipitate the excess iodide (5 drops of 0.5 N $AgNO_3$).

(6) Centrifuge and wash as before saving the supernate and wash.

(7) Make acid with HNO_3 to precipitate the AgCl, centrifuge, and wash the precipitate twice with 3 ml portions of 2 N HNO_3. The precipitate can be plated directly or dissolved in NH_4OH and an aliquot taken.

Remarks: If an appreciable amount of copper is to be dissolved the heat of reaction may drive the chlorine carrier into the receiving vessel before the copper is completely dissolved. If this occurs add 2.5 mg of chlorine carrier as chloride to the water in the receiver and after the copper is in solution add an additional 2.5 mg to the copper solution and distil as stated above. In case bromine is present it may be removed by making the solution 0.5 M in HNO_3 before precipitation, adding 5 mg of Br^- carrier, 0.25 grams of ammonium persulfate and boiling, thus oxidizing the Br^- to Br_2 and volatilizing. The solution should then be reduced with hydrazine and the chlorine precipitated as AgCl.

PROCEDURE 3 - CHLORINE

Source - W. H. Burgus, report LA-1721, 2nd Ed., Cl-1, Aug. 1958

1. Introduction

In the determination of chlorine in the presence of fission products, considerable decontamination is achieved by ferric hydroxide scavenging and by precipitation of silver iodide from ammoniacal medium. Precipitation of silver chloride in the presence of Versene* is then employed, primarily to remove chlorine from alkaline earth metal ions, but also to separate this element from many other activities. After additional decontamination, silver chloride is formed and the chlorine removed as

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*Versene (Bersworth Chemical Co.) is the disodium salt of ethylenediaminetetracetic acid. Versene forms very stable soluble chelates with a large number of metallic ions.

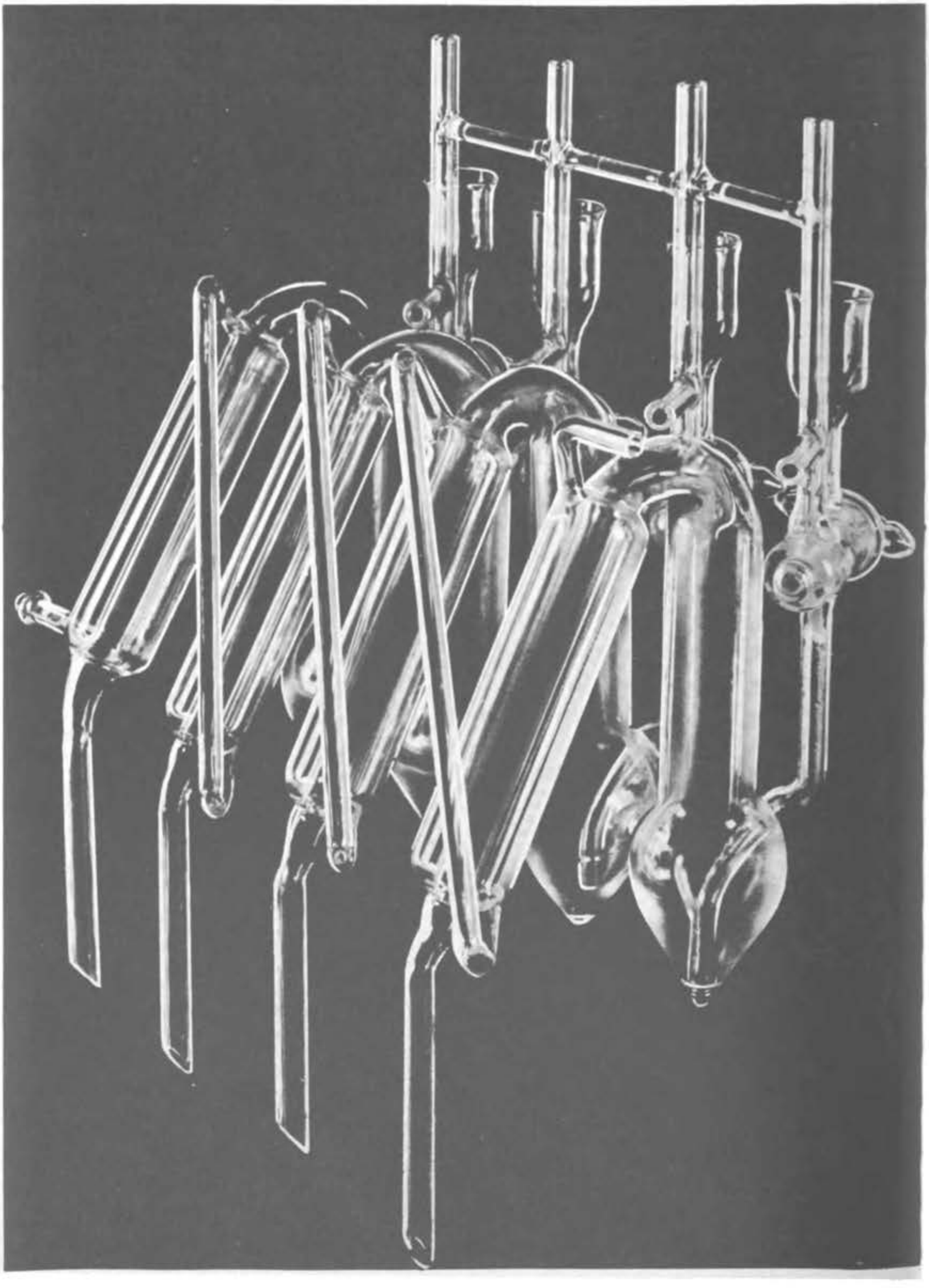
hydrogen chloride by treatment with concentrated sulfuric acid. Chlorine is finally precipitated as the mercury (I) compound, in which form it is counted. The chemical yield is about 75% and a single analysis can be performed in two and one-half hours.

2. Reagents

Cl^- ion carrier: 10 mg Cl^-/ml. (NaCl used as primary standard)
I^- ion carrier: 10 mg I^-/ml. (added as KI in H_2O)
Fe carrier: 10 mg Fe/ml. (added as $Fe(NO_3)_3 \cdot 6\,H_2O$ in very dilute HNO_3)
HNO_3: conc.
HCHO: 37% aqueous solution
NH_4OH: conc.
KOH: 10<u>M</u>
$AgNO_3$: 0.1<u>M</u>
$Hg_2(NO_3)_2$: 0.1<u>M</u> solution in dilute HNO_3.
KNO_2: solid
Versene: disodium salt (analytical reagent grade, Bersworth Chemical Co.)-8% aqueous solution.
CCl_4
C_2H_5OH: absolute

3. Equipment

Centrifuge
Drying Oven
Block for holding centrifuge tubes
Forceps
Mounting Plates
Pipets: assorted sizes
Wash bottle
2", 60° funnels (two per sample)
Ground-off Hirsch funnels: Coors 000A (one per sample)
Filter chimneys (one per sample)
Filter flasks
125-ml separatory funnels (one per sample)
50-ml beakers (one per sample)
40-ml conical centrifuge tubes: Pyrex 8130 (seven per sample)
No. 40 Whatman filter paper (9 cm)
No. 42 Whatman filter circles: 7/8" diameter-weighed
Stirring rods
Special still (see diagram next page)



4. Procedure

Step 1. To the solution containing radioactive chlorine and fission products in a 40-ml conical centrifuge tube, add 1.00 ml of standard NaCl carrier. Then add 4-6 drops of Fe carrier and precipitate $Fe(OH)_3$ by the addition of a slight excess of conc. NH_4OH. Centrifuge, transfer the supernate containing Cl^- ion to a clean centrifuge tube, and discard the precipitate (Note 1).

Step 2. To the supernate add 5 ml of conc. NH_4OH and 4 drops of KI carrier solution. Precipitate AgI by the addition of a slight excess of 0.1M $AgNO_3$ solution. Coagulate the precipitate by heating, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 3. To the supernate again add 4 drops of KI carrier and remove a AgI by-product precipitate as in the previous step. However, this time filter the supernate through No. 40 Whatman filter paper (9 cm) in a 2", 60° funnel to ensure complete removal of AgI.

Step 4. To the filtrate add 5 ml of 8% Versene solution and slowly acidify with conc. HNO_3 to precipitate AgCl. Boil to coagulate the precipitate, centrifuge, and wash the AgCl with 30-40 ml of H_2O containing 2 drops of conc. HNO_3. Discard the supernate and washings.

Step 5. Dissolve the AgCl precipitate in 3 ml of conc. NH_4OH, add 5 ml of an 8% Versene solution, dilute to 30 ml, and reprecipitate AgCl by the addition of conc. HNO_3. Boil to coagulate the AgCl and wash as in the previous step.

Step 6. Dissolve the AgCl in 40 drops of conc. NH_4OH, add 15 ml of H_2O, 10 drops of 10M KOH, and 10 drops of 37% HCHO. Heat to boiling to coagulate the metallic Ag precipitate. Add 4 drops of 0.1M $AgNO_3$ and again remove a Ag precipitate. Filter both Ag precipitates together through No. 40 Whatman filter paper in a 2", 60° funnel, collecting the filtrate in a 125 ml Erlenmeyer flask.

Step 7. Acidify the filtrate with conc. HNO_3, add an additional 2 ml of the acid, and heat to boiling (Note 2). Cool and add 4 drops of KI carrier solution. Transfer to a 125 ml separatory funnel, add 50 ml of CCl_4 and a few crystals of KNO_2. Extract I_2 into the CCl_4 layer and discard. Add three separate additional 10-ml portions of CCl_4, extract I_2, and discard the CCl_4 layer after each extraction.

Step 8. To the remaining aqueous layer add 2-3 cc of conc. HNO_3, transfer to a 40-ml centrifuge tube, and heat to boiling to remove excess NO_2^- ion. Add 4 drops of Fe carrier and precipitate $Fe(OH)_3$ with conc.

NH_4OH. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 9. Again add 4 drops of Fe carrier and remove a $Fe(OH)_3$ scavenger precipitate as in the previous step.

Step 10. To the Cl^--containing supernate add 0.1M $AgNO_3$ to precipitate AgCl. Centrifuge and wash the precipitate as in Step 4.

Step 11. Dissolve the AgCl precipitate in 2 ml of conc. NH_4OH. Wash with several ml of H_2O into a special distilling flask (see diagram of multiple still). Bubble air through the solution to remove most of the NH_4OH. Cautiously add 6 ml of conc. H_2SO_4 (Note 3) and heat until all the HCl has distilled over into a 50 ml beaker containing 20 ml of H_2O.

Step 12. Precipitate Hg_2Cl_2 from the solution of HCl distillate (after adding 1-2 ml of conc. HNO_3) by the dropwise addition of 0.1M $Hg_2(NO_3)_2$ solution. Wash the precipitate with H_2O after filtering on a tared No. 42 Whatman filter circle, 7/8" diameter, using the standard chimney technique. Wash with absolute C_2H_5OH and dry in an oven for 20 minutes at 110°. Cool, weigh, mount, and count (Note 4).

Notes

1. If the radiochlorine is originally in a form other than Cl^- ion or Cl_2, care must be taken to reduce it to one of these forms before beginning the procedure. Otherwise the radiochlorine may be lost as a result of its failure to exchange with Cl^- carrier. The total volume in Step 1 should not exceed 20 ml.

2. Boiling is necessary at this stage to remove most of the volatile HCHO.

3. Addition of conc. H_2SO_4 precipitates AgCl. During distillation continue bubbling air through the solution.

4. Hg_2Cl_2 is used as the compound mounted in preference to AgCl because it does not form agglomerates as does AgCl. $PbCl_2$ is too soluble and therefore not suitable. For counting 4×10^5 y Cl^{36}, a self-absorption curve should be constructed and corrections applied for a 0.72 Mev β^-.

PROCEDURE 4 - BROMINE

Source - W. W. Meinke, report AECD-2738, pp. 95. Aug. 1949

Element separated: Bromine	Procedure by: Goeckermann
Target material: ~ 1 g Bi metal	Time for sep'n. 1-2 hrs.
Type of bbdt: 184" all particles	Equipment required: Centrifuge, tubes, 110° oven

Yield: ~ 60%

Degree of purification: Decontamination factor ~ 10^4 from fission and spallation products.

Advantages: Good yield of pure Br.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg Br^- and I^-, make 1 N in HNO_3, add a few drops of 0.1 M $NaNO_2$, and extract I_2 into equal vol CCl_4.

(2) Add equal vol CCl_4 to aqueous phase and add 0.1 M $KMnO_4$ dropwise until color persists. Make five extractions of Br_2.

(3) Combine CCl_4 layers and wash with 1 N HNO_3 containing $KMnO_4$. Add 10 ml H_2O and 0.1 N $NaHSO_3$ dropwise until both layers are colorless. Wash aq layer with CCl_4.

(4) Make 1 N in HNO_3, add ~ 10 mg I^-, warm a few min to oxidize $SO_3^=$, add few drops 0.1 M $NaNO_2$ and extract I_2 five times with 10 ml CCl_4.

(5) Repeat $KMnO_4$ oxidation and Br_2 extrn and reduction.

(6) Repeat I_2 and Br_2 extrn cycles as needed for purity.

(7) Make last aq soln of Br^- 1N in HNO_3, heat, add 2 ml 0.1 N $AgNO_3$ stir, digest few min, filter, wash three times with 5 ml H_2O, EtOH, and ether, dry 10 min at 110°C. Weigh as AgBr (23.5 mg per 10 mg Br).

Remarks: The bismuth fission work only required three I_2-Br_2 extrn cycles. To prevent possible losses of trace Br during dissolving of the bismuth, one might dissolve the target in 6 N HNO_3 with the carrier Br^- present in a glass still, and distill Br_2 or HBr directly from this soln into H_2O in an ice bath.

PROCEDURE 5 - BROMINE

Source - W. W. Meinke, report AECD-2738, pp. 96. Aug. 1949

Element separated: Bromine

Procedure by: Lindner

Target material: Tantalum

Modified by: Naumann

Type of bbdt: Ta + 350 Mev protons

Time for sep'n: 2 hours

Equipment required: Sep. funnel

Yield: ~ 40%

Degree of purification: excellent - factor of ~ 10^4 from fission and spallation products.

Advantages: Provides for the separation of Br_2 from targets requiring $HF-HNO_3$ mixtures for solution of the target. In these cases glass equipment is impossible and the method of distillation of the halogens is impractical.

Procedure:

(1) Freshly precipitated AgBr (well washed to remove excess Ag^+) containing 10 mgs of bromine as silver bromide is added to 15 mls of 48% HF solution contained in a lusteroid test tube. The target foil is placed in solution and conc. HNO_3 is added as required for solution of the foil. (See (a) under remarks.)

(2) After target has dissolved the solution is allowed to stand for 15 minutes, (See (b) under remarks.) the supernatant target solution is removed, the AgBr washed twice with 10 mls hot water, 10 mls of water is added and the slurry is saturated with H_2S, then centrifuged.

(3) The supernatant solution is boiled to remove H_2S, 10 mgs I^- is added, the solution is made 1 $\underline{N}$ in HNO_3 a few drops of $NaNO_2$ is added and the iodine extracted into 10 mls of CCl_4. (extract a total of 5 times).

(4) 10 mls of CCl_4 is added to the aqueous phase and 0.1 M $KMnO_4$ solution is added until the bromine color persists. Extract Br_2 5 times (total).

(5) Combine the Br_2-CCl_4 extract, wash with 1 $\underline{N}$ HNO_3 containing $KMnO_4$, add 10 mls H_2O and 0.1 $\underline{N}$ $NaHSO_3$ dropwise until both layers are colorless. (See (c) under remarks.) Wash aqueous layer with CCl_4.

(6) Make 1 N in HNO_3 add 10 mgs I^-, warm for a few minutes to oxidize the $SO_3^=$, add a few drops of 0.1 M $NaNO_2$ and extract the I_2 5 times with CCl_4.

(7) Repeat (4) and (5) as needed (A total of 3 times was used for purification above.)

PROCEDURE 5 (Cont'd)

(8) Make last aqueous solution of Br^- 1 N in HNO_3, heat, add 2 mls 0.1 N $AgNO_3$. Stir, digest a few minutes, wash three times with 5 mls H_2O, 5 mls C_2H_5OH, 5 mls ether. Dry for 10 mins at 110°C.

Remarks:

(a) This reaction proceeds rapidly and at no time should there be and excess of HNO_3. Heating is not required and lusteroid tube may be ice cooled if necessary.

(b) Procedure depends upon an equilibration between AgBr and tracer bromide ion in the target solution. If the tracer bromine were in a higher oxidation state this equilibration would be impossible. However, since the Ta is being dissolved it may be assumed reductive conditions exist and all the tracer is in the form of bromine or bromide.

(c) Unless the solution is kept acid MnO_2 will precipitate. The MnO_2 precipitation may also be avoided if the solution is warmed before permanganate addition.

(d) Steps (3) and (9) are R. H. Goeckermann's procedure for bromine.

(e) I_2 might also be separated by this procedure.

PROCEDURE 6 - BROMINE

Source - W. W. Meinke, report AECD-2738, pp. 98. Aug. 1949

Element separated: Bromine	Procedure by: Newton
Target material: Thorium metal (.1-1 gm)	Time for sep'n: ~ 1 hr.
Type of bbdt: 60" metal	Equipment required: Standard

Yield: ~ 50%

Degree of purification: ~ 10^6 except from I^- (~ 10^4 from I^-)

Procedure: The Th metal is 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. Sample added to 15 ml 1 N HNO_3 in 50 ml separatory funnel. Add 10 mg Br^- carrier and 10 mg I^- carrier.

(1) Add $KMnO_4$ (0.1N) dropwise until color persists (15 drops). Make 5 successive extractions with CCl_4. Discard aqueous. To CCl_4 layer add 10 ml water and 0.1 N $NaHSO_3$ until CCl_4 layer colorless on shaking. Discard the CCl_4.

(2) To aqueous add 2 ml HNO_3 and 10 mg I^-, add 4 drops of 0.1 M $NaNO_2$. Extract five times with CCl_4. Add more I^- and repeat extraction with four more portions of CCl_4.

(3) Add $KMnO_4$ to oxidize Br^-. Extract five times with CCl_4.

PROCEDURE 6 (Cont'd)

(4) Extract CCl_4 with $NaHSO_3$. Add Ag^+ to ppt AgBr. Filter, wash three times with 5 ml H_2O and three times with 5 ml EtOH. Dry at 110°, 10 min and weigh. 10 mg Br^- = 23.5 mg AgBr.

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

PROCEDURE 7 - BROMINE

Source - Glendenin, Edwards and Gest, N.N.E.S., Vol. 9, Book 3, pp. 1451

1. Introduction

Bromine is separated from the other fission products by the reduction of BrO_3^- carrier to Br^- with H_2S, followed by oxidation to Br_2 with $KMnO_4$, and extraction into CCl_4. The Br_2 is removed from the CCl_4 by shaking with water containing $NH_2OH.HCl$. The aqueous solution is then purified[34] by two more CCl_4 extraction cycles, using $KMnO_4$ for oxidation to Br_2 and using $NaHSO_3$ for reduction to Br^-. The bromine is finally precipitated as AgBr for weighing and counting.

The reduction of BrO_3^- to Br^- with H_2S ensures the interchange of radiobromine with the carrier.[35] Failure to achieve a complete interchange has been observed in previous methods of bromine separation.[36,37] The use of $NH_2OH.HCl$ to reduce Br_2 to Br^- in the first extraction cycle helps to decontaminate the bromine from iodine, since $NH_2OH.HCl$ does not reduce I_2 to I^-. Contamination by other fission activities, including iodine, is negligible. The chemical yield is 50 per cent or more, and the time required for a complete analysis is about 1 hr.

2. Procedure

Step 1. To not more than 5 ml of a solution of neutron-irradiated uranyl nitrate (Note 1) in a 50-ml centrifuge tube, add 20 mg of bromine carrier as BrO_3^- and 10 mg of iodine carrier as IO_3^-. Pass in H_2S for 1 to 2 min (Note 2), boil briefly to expel the H_2S, cool, and transfer the solution to a 60-ml separatory funnel.

Step 2. Add 1 ml of 6M HNO_3 and a few drops of 1 M $KMnO_4$ (Note 3), extract the Br_2 into 10 ml of CCl_4, and discard the aqueous layer.

Step 3. Shake the CCl_4 layer with 10 ml of H_2O containing 1 ml of 1M $NH_2OH.HCl$, and discard the CCl_4.

Step 4. Repeat Step 2.

Step 5. Shake the CCl_4 layer with 10 ml of H_2O containing a few drops of 1M $NaHSO_3$, and discard the CCl_4.

Step 6. Repeat Step 2.

Step 7. Repeat Step 5.

Step 8. Add 1 ml of 6M HNO_3, and heat nearly to boiling (Note 4). Add 2 ml of 0.1M $AgNO_3$ drop by drop with stirring and digest the precipitate of AgBr for a few seconds. Filter with suction on a weighed filter-paper disk (Note 5) in a small Hirsch funnel, and 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 AgBr, and mount.

Notes. 1. The sample solution should be neutral or slightly acidic.

2. The presence of HNO_3 in the sample will cause the formation of free sulfur at this point. This does no harm, since the sulfur is left behind during the CCl_4 extraction cycles.

3. Sufficient $KMnO_4$ should be added to maintain a permanent purple color.

4. The solution is acidified and heated to expel SO_2, which might interfere in the AgBr precipitation.

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

PROCEDURE 8 - BROMINE

Source - R. Overstreet and L. Jacobson, N.N.E.S., Vol. 9, Book 3, pp. 1453

Selenium metal was fused on a copper cyclotron target and bombarded in a bell jar with deuterons at the Berkeley cyclotron. The selenium is dissolved in conc. HNO_3. The solution is diluted to 6M, and the acid is distilled from the solution. The distillate, containing Br^{82}, is collected in CCl_4, which is then washed three times with distilled water. Sufficient Cl_2 gas is added to the CCl_4 to produce a definite yellow color, and the mixture is placed in direct sunlight for at least 1 hr. At the end of this period the CCl_4 mixture is extracted with an excess either of Na_2SO_3 or of $Na_2S_2O_3$ to give a solution of tracer bromine free of significant amounts of bromine carrier.

PROCEDURE 9 - BROMINE

Source - R. R. Edwards and H. Gest, N.N.E.S., Vol. 9, Book 3. pp 1454

In connection with studies on the chemical effects associated with the formation of bromine from the decay of selenium[38] on the behavior of of bromine at tracer concentrations,[39] several interesting reactions were studied which are reported briefly here.

Tracer bromine solutions were prepared by the neutron irradiation of degassed $KBrO_3$ and the extraction of the water solution by CCl_4 in the presence of HNO_3 and $KMnO_4$. About 60 per cent of the 34 h Br^{82} is found in the CCl_4 layer. Reextraction into a water layer with $NaHSO_3$ gives a solution of Br^- concentration of the order of $10^{-10}M$, since Ag^+ gives no precipitate or centrifugable colloid.[39] A large fraction (about 70 per cent) of the bromine activity can be extracted from the CCl_4 solution by water, presumably because of the hydrolysis of Br_2 to Br^- and BrO^-. An appreciable fraction (about 16 per cent) is not extracted by water but is extracted by $NaHSO_3$-KBr solution, as found by DeVault and Libby.[40] This fraction also reacts in the absence of light with ethylidene bromide, CH_3CHBr_2, a reaction characteristic of bromine atoms and not of Br_2. This fraction is provisionally designated as "atomic" bromine, although atomic bromine is not expected to be present in appreciable amounts even in these dilute solutions unless it is highly stabilized by complex formation with the solvent. In addition, a small fraction of the activity is bound by the purified CCl_4, and a roughly equal fraction is lost, perhaps to the wall; these losses may be due to β-radiation effects. Extensive studies of the reactivity of the tracer are presented elsewhere.[39]

With the aid of water solutions of the tracer extracted from the CCl_4 solution, it was shown that 96 to 99 per cent of the activity is collected by freshly prepared AgBr in 10 to 45 min of stirring. Kolthoff and O'Brien[41] have shown that freshly precipitated AgBr exchanges rapidly with Br^- at ordinary concentrations; this experiment shows that BrO^- also exchanges readily at concentrations below $10^{-10}M$.

Bromine tracer does not exchange appreciably with 0.13M $KBrO_3$ after standing for 10 to 100 min at room temperature in a neutral solution, as shown by the complete recovery of the activity with added AgBr precipitate.

PROCEDURE 10 - IODINE

Source - W. W. Meinke, report AECD-3084, pp. 21. March, 1951

Element separated: Iodine

Procedure by: H. D. Sharma

Target material: Te (2 lbs.)
From natural radioactive Te (?)

Time for sep'n: 3 hours

Equipment required: Standard

Yield: 60%

Degree of purification: At least 10^6 from Te

Procedure:

(1) Te metal was oxidized by conc. HNO_3 to TeO_2 which was fused with NaOH. The fused mass was dissolved in water.

(2) 10 mg of I^- and 20 mg Br^- were added as carriers to the solution. $AgNO_3$ was added slowly to excess to ppt AgI and AgBr, avoiding precipitation of Ag_2O.

(3) Ppt was obtained by centrifuging the solution and then treating with 1 gm of $K_2Cr_2O_7$ and 15 ml of H_2SO_4. The mixture was digested for 30 minutes at 95°C.

(4) A stream of air was bubbled through the solution for 15 minutes and then the solution was cooled and treated with conc. Na_2SO_3 solution slowly until a faint odor of SO_2 remained after standing 10 minutes.

(5) AgI was ppted by adding $AgNO_3$ to the mixture.

Remarks:

Iodine was milked from natural Te.

See: Scott's Standard Methods of Chemical Analysis, page 276.

PROCEDURE 11 - IODINE

Source - W. W. Meinke, report AECD-2738, pp. 161. Aug. 1949

Element separated: I ($\sim 10^{-6}$ barns cross section)

Procedure by: Marquez

Target material: Sn (~ 1 gm)

Time for sep'n: 50 min.

Yield: 70-80%

Equipment required:
100 cc distillation flask
separatory funnels
centrifuge tubes

Type of bbdt: 184" α and p

Degree of purification: Less than 1% impurity in final I sample.

Advantages: Fast. Makes possible sep'n of a very small amount of pure I from large amounts of other activities.

PROCEDURE 11 (Cont'd)

Procedure:

(1) Add 10 mg I^- carrier and target foil to distillation flask.
(2) Add ~ 15 ml conc. H_2SO_4; (H_2SO_4 should be cold) to dissolve the Sn.
(3) Dissolve Sn and distill simultaneously, collecting I_2 in 0.5-1<u>N</u> NaOH solution.
(4) Acidify with H_2SO_4 until iodine turns brown and oxidize with HNO_2, ($NaNO_2$ in acid solution). Extract with equal volume CCl_4.
(5) Wash I^- into NaOH solution.
(6) Repeat NaOH-CCl_4 cycles as many times as wished. (Three cycles gave purity listed above.)
(7) Acidify last NaOH solution with H_2SO_4 and reduce with SO_2 gas. Blow air through solution to expel most of SO_2. Add excess Ag^+ and a few drops of conc. HNO_3.
(8) Heat in water bath and filter.
(9) Plate and count as AgI.

Remarks:

Most of the loss in this procedure comes in the distillation process. Ice cold H_2SO used in (2) to allow assembly of distillation apparatus before solution of target starts.

SO_2 solutions can be used to collect the I_2 from the distillation. The solution is then oxidized with HNO_2 and the I_2 extracted went equal volume of CCl_4. The I_2 washed out of the organic layer into SO_2 solution and the cycle repeated. This SO_2 procedure is troublesome in the experiments above because the solution develops a gas pressure during the extractions.

PROCEDURE 12 - IODINE

Source - W. W. Meinke, report AECD-2738, pp. 162. Aug. 1949

Element separated: Iodine
Target material: Sb (~ 500 mg)
Type of bbdt: $60''$ α particles

Procedure by: Marquez
Time for sep'n: ~ 40 min.
Equipment required:
100 distillation flasks
sep funnels and centrifuge tubes

Yield: 80% or higher

Degree of purification: At least a factor of 10^4 from other activities present.

Advantages: Fast and good separation.

Procedure:

(1) Add target, 10 mg I^- carrier, 10-15 ml of saturated tartaric acid and 10-15 ml of ice cold HNO_3 to distillation apparatus.

(2) Distil and collect I_2 in 0.5-1 N NaOH.

(3) Acidify with H_2SO_4 until iodine turns brown and oxidize with HNO_2, ($NaNO_2$ in acid solution). Extract with equal volume CCl_4.

(4) Wash I^- into NaOH solution.

(5) Repeat NaOH-CCl_4 cycles as many times as wished. (Three cycles gave purity listed above.)

(6) Acidify last NaOH solution with H_2SO_4 and reduce with SO_2 gas. Blow air through solution to expel most of SO_2. Add excess Ag+ and a few drops of conc. HNO_3.

(7) Heat in water bath and filter.

(8) Plate and count as AgI.

Remarks:

Most of the loss in this procedure comes in the distillation process.

Ice cold HNO_3 used in (1) to allow assembly of distillation apparatus before solution of target starts.

Solution of Sb in aqua regia interferes with I_2 extraction.

An I^- sample could be obtained in 15-20 min by ppting the AgI directly from the distillate of (2). The radioactive purity of the sample, however, will not be as high as above.

SO_2 solution can be used to collect the I_2 from the distillation. The solution is then oxidized with HNO_2 and the I_2 extracted with equal volume of CCl_4. The I_2 washed out of the organic layer into SO_2 solution and the cycle repeated.

PROCEDURE 13 - IODINE

Source - W. W. Meinke, report AECD-2738, pp. 163. Aug. 1949

Element separated: Iodine	Procedure by: Goeckermann
Target material: ~ 1 g Bi metal	Time for sep'n: ~ 2 hrs.
Type of bbdt: 184" all particles	Equipment required: Distillation flask, centrifuge, tubes, ice, 110° oven.

Yield: Approx. 40%

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

Advantages: Fair yield of pure I with little if any non-exchange trouble.

Procedure:

(1) Place target in glass still, add 10 mg I^- and 10 ml 6N HNO_3, warm to dissolve. When entirely dissolved, distill over the I_2 and a few ml HNO_3 into H_2O in an ice bath.

(2) Reduce I_2 with a minimum of $NaHSO_3$ in the cold, adjust, to 0.5N HNO_3, add a few drops 0.1M $NaNO_2$, and extract I_2 into an equal volume of CCl_4. Extract aqueous with second portion CCl_4. Wash CCl_4 with dilute HNO_3.

(3) Shake CCl_4 with 10 ml H_2O, adding $NaHSO_3$ until both phases colorless. Wash aqueous with CCl_4.

(4) Repeat extraction cycle several times.

(5) Make last aqueous I^- solution 0.5N in HNO_3, heat to boiling, add 2 ml 0.1N $AgNO_3$, digest, filter, wash three times with H_2O, three times with 5 ml C_2H_5OH, three times with 5 ml ether, dry 10 min at 110°C. Weigh as AgI (18.50 mg per 10 mg I).

Remarks: Active iodine formed as periodate may not exchange with the carrier by this method, although the I yields were not abnormally low. Reducing condition probably prevail during dissolution of the target.

PROCEDURE 14 - IODINE

Source - W. W. Meinke, report AECD-2738, pp. 164. Aug. 1949

Element separated: Iodine	Procedure by: Newton
Target material: Throium metal (.1-1 gm)	Time for sep'n.: 1 hr
Type of bbdt: 60" α's	Equipment required: Standard
Yield: 90%	

Degree of purification: 10^6

Procedure: The Th metal is 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.

Procedure:

(1) Add sample to 10 ml 2 M Na_2CO_3(1). Add 20 mg I^- in 60 ml sep funnels. Add 2 ml 2.5% NaOCl(2). Heat. Acidify with 3 ml conc. HNO_3, add 3 ml 1 M $NH_2OH \cdot HCl$(3) Extract with 10 ml CCl_4.

(2) Shake with 10 ml H_2O containing a few drops $NaHSO_3$ until both phases colorless.

(3) To water add 1 ml 6 N HNO_3 and a few drops of 1 M $NaNO_2$. Extract into CCl_4.

(4) Repeat (2).

(5) Add 1 ml 6 $\underline{N}$ HNO_3. Heat to boiling. Add 2 ml 0.1 $\underline{N}$ $AgNO_3$. Stir and digest. Filter on tared filter paper. Wash three times with 5 ml H_2O, three times with 5 ml EtOH and three times with 5 ml Et_2O. Dry at 110°C for 10 min. Weigh as AgI.

Remarks: 10 mg I = 18.42 mg AgI

(1) If Bi and La present add 1 ml of 10% tartaric acid and 19 $\underline{M}$ NaOH.

(2) Oxidize I^- to IO_4^-. Solution must be heated, preferably boiled 5 minutes for complete exchange to occur.

(3) Reduce IO_4^- to I_2.

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

Preparation of carrier solution: Dissolve 13 gms KI in water containing a trace of $NaHCO_3$. Dilute to one liter.

Standardization: Take 5 ml carrier solution in beaker. Add 50 ml H_2O and 1 ml 6 $\underline{N}$ HNO_3. Heat nearly to boiling and add 5 ml 0.1 $\underline{N}$ $HgNO_3$ with stirring. Digest 1 minute. Filter into a sintered glass crucible, wash three times with H_2O, three times with 95% EtOH. Dry at 110°C and weigh as AgI.

PROCEDURE 15 - IODINE

Source - L. E. Glendenin and R. P. Metcalf, N.N.E.S., Vol. 9, Book 3, pp 1625

1. Introduction

A widely used method for direct separation of radioactive iodine from the other fission products is the CCl_4 extraction of iodine in the elementary state.[42,43] Extensive work on the problem of interchange[3] has shown that preliminary steps to effect complete interchange between tracer iodine and carrier iodine are required before the separation by CCl_4 extraction can be made. A satisfactory method of achieving the required interchange was developed;[44] it consists in the oxidation of I^- carrier to IO_4^- (periodate) with NaClO in alkaline solution. This reaction has been incorporated into the present procedure. After the interchange reaction the solution is acidified, the IO_4^- is reduced to I_2 with hydroxylamine hydrochloride ($NH_2OH.HCl$), and the I_2 is extracted with CCl_4. The I_2 is removed from the CCl_4 by shaking with water containing $NaHSO_3$ and is then purified by another CCl_4 extraction cycle, in which $NaNO_2$ is used for the oxidation of I^- to I_2 and $NaHSO_3$ is used for the reduction of I_2 to I^-.

The iodine is finally precipitated as AgI for weighing and counting. Contamination by other fission activities, including bromine, is negligible. The complete procedure, together with a discussion of the development work, is given below.

2. Preparation and Standardization of Carrier

Dissolve 13 g of reagent - grade KI in water containing a few milligrams of $NaHCO_3$, and dilute to 1 liter. This solution contains 10 mg of iodine per milliliter.

Pipet 5 ml of the carrier solution into a beaker, add about 50 ml of H_2O and 1 ml of 6M HNO_3, and heat nearly to boiling. Add 5 ml of 0.1M $AgNO_3$ drop by drop with continuous stirring, digest the precipitate for about 1 min, and filter quantitatively on a weighed sintered-glass crucible with suction. 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 the 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 AgI.

3. Procedure

Step 1. Add to the sample of fission products (containing not more than 5 g of uranyl nitrate) in a 60-ml separatory funnel about 10 ml of 2M Na_2CO_3 (Note 1) and 2 ml of I^- carrier. Add 1 ml of 5 per cent NaClO, mix well (Note: It is desirable to give the NaClO time to oxidize radioiodine species fully, or better to heat), and acidify the solution by slowly adding 3 ml of conc. HNO_3. Add 3 ml of 1M $NH_2OH.HCl$, and extract the I_2 into 10 ml of CCl_4. Discard the aqueous layer.

Step 2. Shake the CCl_4 layer with 10 ml of H_2O containing a few drops of 1M $NaHSO_3$ until both phases are colorless, and discard the CCl_4.

Step 3. Add 1 ml of 6M HNO_3 and a few drops of 1M $NaNO_2$, extract the I_2 into 10 ml of CCl_4, and discard the aqueous layer.

Step 4. Repeat step 2.

Step 5. Add 1 ml of 6M HNO_3, and heat nearly to boiling (Note 2). Add 2 ml of 0.1M $AgNO_3$ drop by drop with stirring, and digest the precipitate of AgI for a few seconds by gentle boiling and brisk stirring (Note 3). Filter with suction onto a weighed filter-paper disk (Note 4) 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 AgI, and mount.

Notes. 1. Uranyl nitrate hexahydrate (either as the solid or in solution) is readily soluble in Na_2CO_3 solution by the formation of the carbonate complex. If there is much free acid in the uranyl nitrate, the addition of more Na_2CO_3 and gentle heating may be required to effect complete solution.

2. The solution is acidified and heated to expel SO_2 which might interfere in the AgI precipitation.

3. Silver iodide tends to form both a milky suspension and large clumps of precipitate. The digestion procedure aids in coagulating the suspension and also in breaking up the large particles of precipitate.

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

4. Discussion

Previous methods of determining fission-iodine activities, involving the use of carriers[2] in the form of I^- and employing oxidation-reduction reactions in acid solution to obtain I_2 for separation by extraction, have been shown to give low and erratic yields,[44-46] evidently owing to incomplete interchange between the radioiodine and the carriers. The interchange tests on previous methods of iodine separation consisted in preparing a stock solution of 77 h Te, determining the 2.4 h I daughter activity at equilibrium by counting an aliquot of the stock solution through sufficient aluminum to absorb the softer β radiation of the 77 h Te, and comparing this activity with the 2.4 h I activity obtained by various methods of iodine separation. In these tests it was found that the earlier methods did not effect either complete or reproducible interchange between radioactive iodine and carrier iodine. For example, the procedure involving the addition of iodine carrier as IO_4^- and reduction to I^- with $NaHSO_3$ in dilute acid solution was found to give incomplete separations of 2.4 h I from the stock solution, varying from 65 to 95 per cent. From these interchange tests it was evident that the usual methods of iodine separation do not give a complete removal of radioiodine from fission material.[44,46]

Work on the development of a procedure that would effect a fast and complete interchange of radioiodine with carrier iodine was carried out, and a satisfactory method was found in the oxidation of I^- to IO_4^- by NcClO in an alkaline solution. This reaction was shown to give complete and rapid interchange[44] by the 2.4 h I tracer tests mentioned above and has been incorporated in the procedure described in this paper. The difficulty of working in an alkaline solution in the presence of UO_2^{++} has been circumvented by use of the carbonate complex to prevent precipitation of uranium.

Separate tracer tests with various fission activities have not been made, but the procedure has been used in a great deal of work on short-lived iodine activities,[47] with no evidence of contamination by other fission activities, including the most probable contaminant, bromine. Two separations from bromine are afforded in the procedure: one separation is given by the reduction to Br^- with hydroxylamine while I_2 is being extracted, and the other separation is given by the extraction of I_2 after oxidation with HNO_2 (this does not oxidize Br^-). Moreover, the longest-lived bromine activity in fission with a significant yield is 2.4 h Br^{83}; hence bromine activity is not present in fission-product solutions that are more than a day old.

The iodine procedure can be adapted readily to a tandem method determining iodine and bromine. In this case Br^- carrier is also added in step 1 (see Sec. 3), oxidized to BrO_3^- by the NaClO, and reduced to Br^- by the hydroxylamine. The I_2 is then extracted with CCl_4, and the Br^- in the aqueous layer is oxidized to Br_2 with $KMnO_4$ and is extracted into CCl_4. The bromine can then be purified, as in the case of iodine (steps 2 and 4), by another CCl_4 extraction cycle, in which $KMnO_4$ is used in dil. HNO_3 for the oxidation of Br^- to Br_2 and hydroxylamine is used for the reduction of Br_2 to Br^-. The bromine is precipitated as AgBr for weighing and counting,[48,49] as in the case of iodine (step 5). The separation from iodine should be excellent, since $KMnO_4$ oxidizes I^- to IO_3^- and thus prevents its extraction with Br_2 and since hydroxylamine reduces IO_3^- to I_2 and prevents its extraction with Br^-.

PROCEDURE 16 - IODINE

Source - Katcoff, Dillard, Finston, Finkle, Seiler and Sugarman, N.N.E.S., Vol. 9, Book 3, pp 1635

1. Introduction

The procedure presented in this paper was developed to separate iodine formed in the fission of uranium metal. Complete exchange of the radioiodine with carrier I^- is expected, since the iodine activity formed in uranium metal is in a highly reducing medium and therefore is almost certainly present as I^- ion, which should exchange rapidly with I^- carrier during solution of the metal in 12 M HCl. After the uranium metal is completely dissolved, U(IV) and I^- are oxidized to UO_2^{++} and IO_3^- with an excess of $KMnO_4$. The IO_3^- is then reduced to I_2 with $NH_2OH \cdot HCl$ and is removed from the other fission elements by distillation into a NaOH solution. The distillate is acidified, and I_2 is removed by extraction with CCl_4. The I_2 is removed from the CCl_4 by shaking with aqueous $NaHSO_3$ and is then purified by two more CCl_4 extractions, in which $NaNO_2$ is used for the oxidation of I^- to I_2 and $NaHSO_3$ is used for the reduction of I_2 to I^-. The iodine is finally precipitated as PdI_2 for weighing and counting.

2. Procedure

Step 1. Transfer a suitable sample of irradiated uranium metal to a distilling flask that contains 2 ml of KI (I^- concentration of 10 mg/ml) carrier. Add 60 ml of conc. HCl to dissolve the metal. To the small residue of carbide and oxide that remains, add 40 ml of 1M $NaNO_2$ to complete the solution (Note 1). The exit tube of the distilling flask is extended into 20 ml of 6N NaOH solution, and a slow stream of air is passed continuously through the solution during this step (Note 2).

Step 2. Add the NaOH from the trap to the solution in the distilling flask, and stir the solution. Refill the trap with 20 ml of fresh 6N NaOH. Add an excess of sat. $KMnO_4$ to the solution to oxidize U(IV) and I^- to UO_2^{++} and IO_3^-. Add 1.5M $NH_2OH \cdot HCl$ slowly until the solution becomes light yellow, and then add 20 ml more. Heat the solution to distill the I_2 into the NaOH solution.

Step 3. Acidify the distillate, and extract the I_2 with 10 ml of CCl_4. Discard the aqueous layer.

Step 4. Shake the CCl_4 layer with 10 ml of H_2O containing a few drops of 1 M $NaHSO_3$ until both phases are colorless, and discard the CCl_4 layer.

Step 5. Add 1 ml of 6N HNO_3 and a few drops of 1M $NaNO_2$, extract the I_2 into 10 ml of CCl_4, and discard the aqueous layer.

Step 6. Repeat step 4.

Step 7. Heat the aqueous layer and add slowly 2 ml of $Pd(NO_3)_2$ (10 mg/ml) to precipitate PdI_2. Filter with suction on a weighed filter-paper disk in a small Hirsch funnel, and 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 PdI_2, and mount.

Notes. 1. Under these conditions the $NaNO_2$ does not liberate I_2.

2. Any vapors of I_2 or HI that may come over are caught in the NaOH solution.

3. Discussion

Previous methods of determining fission-iodine activities have been shown to give low and erratic yields, evidently because of incomplete interchange between the tracer iodine and the carrier iodine.[50,51] The procedure described above was observed to give a fast and apparently complete interchange in the determination of the fission yield[52] of 6.7 h I. The method is dependent, however, on the use of irradiated uranium metal dissolved in HCl and $NaNO_2$ to provide complete interchange; it cannot be used on other fission-product sources.* The problem of complete interchange is avoided in this case, since the active iodine is in a reducing medium and is probably present as I^- ion, which exchanges rapidly with I^- carrier.

Contamination by other fission activities, including bromine, is negligible. Separation from bromine is afforded in the procedure by reduction with $NH_2OH \cdot HCl$ to Br^- while the I_2 is being extracted, and by the extraction of I_2 after oxidation with $NaNO_2$, which does not oxidize Br^-. The chemical yield for the procedure is approximately 60 per cent.

PROCEDURE 17 - IODINE

Source - R. Overstreet and L. Jacobson, N.N.E.S., Vol. 9, Book 3, pp 1638

Tellurium metal is fused on a copper target and is bombarded with deuterons in a bell jar in the cyclotron. The tellurium is dissolved in 6N HNO_3 and the solution is distilled. The distillate, containing the radioactive 13.0 d I^{126}, 25 m I^{128}, 12.6 h I^{130}, and 8.0 d I^{131}, is collected in CCl_4, which is then washed three times with distilled water. Sufficient Cl_2 gas is added to the CCl_4 to produce a definite yellow color, and the mixture is placed in direct sunlight for at least 1 hr. At the end of this period the CCl_4 mixture is extracted with an excess of either Na_2SO_3 or $Na_2S_2O_3$ to give a solution of tracer iodine free of significant amounts of inactive iodine carrier.

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*A procedure developed (Glendenin, Metcalf, Novey, and Coryell, N.N.E.S., Vol. 9, Book 3, pp 1629) for use with irradiated uranyl nitrate is presented in N.N.E.S., Vol. 9, Book 3, pp 1625 by Glendenin and Metcalf (Procedure 15).

PROCEDURE 18 - IODINE

Source - D. S. Ballantine, N.N.E.S., Vol. 9, Book 3, pp 1639

Stable tellurium is irradiated with pile neutrons to produce 25m Te^{131} and 30 h Te^{131m} by the (n,γ) reaction; the radioactive tellurium then decays to 8 d I^{131}. After a suitable decay period the radioactive iodine is oxidized to IO_3^- during the solution of the irradiated tellurium sample in a mixture of 18N H_2SO_4 and 50 per cent CrO_3 in a 2 to 1 proportion. The I^{131} activity, after the reduction of IO_3^- to I_2 by the addition of oxalic acid, is separated from the tellurium by distillation into a trap containing dil. NaOH. The general features of this method were suggested by I. L. Chaikoff.

An alternative source of I^{131} is the HNO_3 condensate from the dissolution of neutron-activated uranium metal. The reduction of the iodine in the HNO_3 solution is not practical because the NO evolved carries with it much of the iodine. The iodine is separated from HNO_3 by oxidizing all the active iodine to IO_3^-, in which state it is not volatile, and removing the HNO_3 by distillation. The oxidation is performed in a mixture of 18N H_2SO_4 and 50 per cent CrO_3 in a 2 to 1 proportion. The IO_3^- is then reduced to I_2 with oxalic acid and is removed from the other fission elements by distillation.

2. Separation of I^{131} from Tellurium

After the irradiation of elementary tellurium in the pile and a suitable delay (to allow the 30 h Te^{131m} to decay to I^{131}), the sample is placed in a distillation flask equipped with a reflux condenser. To this are added 18N H_2SO_4 and 50 per cent CrO_3 in a 2 to 1 proportion, and the mixture is digested on a steam bath for 1 hr. (A 15-g sample requires about 100 ml of H_2SO_4 and about 50 ml of CrO_3 solution.) In this step the tellurium is dissolved and the radioactive iodine is oxidized to IO_3^-. After the solution has been allowed to cool to room temperature, about 50 to 60 g of oxalic acid and 50 to 75 ml of 18N H_2SO_4 are added. A reaction starts slowly, but soon there is frothing, and the reaction becomes vigorous for a minute or more. If sufficient oxalic acid has been added, the solution will turn from a dark-brown color to a dark-green color as the chromate is reduced to chromic ion. If the solution is not definitely green, more oxalic acid should be added.

When the reduction is complete, the actual distillation of the iodine is begun. The apparatus consists of the original flask used in the dissolving step, a condenser, a receiving vessel, and a trap containing dil. NaOH. Any vapor that fails to condense in the condenser is bubbled through the NaOH trap so that none of the iodine can escape.

The progress of distillation can be observed by placing a direct-reading radiation meter under the receiving vessel and observing the increase in radiation intensity as the iodine is distilled. About 60 per cent of the total activity can be obtained in the first 15 or 20 ml of the distillate. This first distillate is approximately 0.01 M in H_2SO_4, as measured by titration with standardized NaOH, and less than 0.001 N in reducing agents, as determined by titration with standardized permanganate solution. The solid materials usually total about 2 to 3 mg, and the radiochemical purity exceeds 99 per cent.

Further distillation will yield 25 to 30 per cent more of the total iodine, but this is obtained slowly and in a volume of 100 to 200 ml. This can be concentrated, however, by making the distillate basic with NaOH and heating to dryness, then acidifying with H_2SO_4 and oxalic acid and redistilling. The yield on this second distillation runs about 90 per cent in a volume of about 20 ml. This distillate is about 0.05N to 0.1N in H_2SO_4 but is similar to the first distillate in that it is about 0.001N in reducing agents and contains only a few milligrams of solid material.

To date, the largest amount of tellurium that has been used is a 50-g sample. This 50-g sample at saturation, followed by 2 days of decay, yielded 75 millicuries in the first distillate and about 30 millicuries in the second distillate. By correcting for decay it was found that, at the time the tellurium was removed from the pile, the total iodine produced amounted to about 125 millicuries.*

3. Recovery of I^{131} from HNO_3 Solution

When neutron-activated uranium metal is dissolved in hot conc. HNO_3 and the fumes are condensed, the solution, about 10N in HNO_3 is found to contain an appreciable fraction of the fission-iodine activity together with traces of iron and chromium from the stainless-steel equipment. Reduction of the iodine to the elementary state and extraction with

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*Editors' Note: Independent study of the same type of procedure is reported in detail by A. W. Kenny and W. T. Spragg (J. Chem. Soc., 1949: S323).

CCl_4 is not practical. For easy handling, the HNO_3 is distilled off while the iodine is maintained in the iodate state.

The HNO_3 condensate is placed in a distilling flask equipped with a condenser and a receiving vessel. One-to-one H_2SO_4 and 50 per cent CrO_3 are added in 2 to 1 proportion until the characeristic dark chromate color is obtained. The mixture is then distilled to remove all the HNO_3 until white fumes of H_2SO_4 appear. The solution is then cooled, and about 10 g of oxalic acid and about 25 ml of 18N H_2SO_4 are added to reduce all the CrO_3. This mixture is distilled in the manner described above. About 80 per cent of the total activity is thus obtained in a volume of 25 ml. This distillate is about 0.05N to 0.1N in H_2SO_4 and less than 0.001N in reducing agents, and it contains only a few milligrams of solid material. The radiochemical purity is more than 99 per cent.

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