gives a positive uranium test and should never be used.

## CONCLUSIONS

On the basis of the tests several conclusions were reached relative to the fixing of natural water samples for uranium analysis.

The data in Table I indicate that the loss of uranium, by adsorption on glass, even from distilled water, is relatively slow. Apparently most salts tend to minimize this loss by saturating the available positions on the glass surface and by providing anions to complex the uranium.

There appears to be little difference between polyethylene and borosilicate glass bottles with respect to adsorption loss of uranium (Table I).

The test with distilled water (No. 1) in Table II indicates that some soils can adsorb considerable amounts of uranium. The possibility exists that in turbid streams the greater part of the total uranium content could be lodged on suspended matter.

Some anions, notably bicarbonate,

exhibit a complexing action which may minimize uranium adsorption by soil (Table II).

Acids are not good fixing agents for uranium in the presence of suspended matter, because considerable concentrations of quenchers may be leached from the solid matter. Samples 5 and 6 (Table II) gave strong qualitative tests for manganese and copper, while only traces of copper and no manganese could be detected in sample 1. The high concentration of quenchers in sample 6 ( $\phi = 0.3$ ) probably accounts for the high error in this uranium result.

In Table III the loss of uranium caused by coprecipitation with ferric hydroxide was investigated. The two samples where no complexing agent was present (1 and 2) showed high loss of uranium. In the presence of sufficient carbonate or bicarbonate, the uranium loss can be held to a minimum. This is in line with the findings of Guttag and Grimaldi (3), who showed that only 0.01  $\gamma$  of uranium was lost when carbonate was used to precipitate 6.5  $\gamma$  of iron from a 5-ml. solution containing 2.25  $\gamma$  of uranium.

## REFERENCES

- REFERENCES
  (1) Fields, P. R., Pyle, G. L., ANAL. CHEM. 23, 1004 (1951).
  (2) Fletcher, M. H., U. S. Geol. Survey, Bull. 1006, 51-68 (1954).
  (3) Guttag, N. S., Grimaldi, F. S., Ibid., 1006, 111-19 (1954).
  (4) Koczy, G., Akad. Wiss. Wien, Math.-naturwiss. Kl., Sitzber., Abt. 11a, 158 Band, 1-5 Heft, 113-22 (1950).
  (5) Milkey, R. G., ANAL. CHEM. 26, 1800 (1954).
  (6) Price, G. R., Ferretti, R., Schwartz, S., Ibid., 25, 322 (1953).
  (7) Rodden, C. J., "Analytical Chemistry of the Manhattan Project," McGraw-Hill, New York, 1950.
  (8) Smith, A. P., Grimaldi, F. S., U. S. Geol. Survey, Bull. 1006, 125-31, (1954).
  (9) Stourner, P. F. Wood, W. H. Coota (1954)
- (9) Stevens, R. E., Wood, W. H., Goetz, K. G., Horr, C. A., Seventh Pitts-burgh Conference on Analytical Chemistry and Applied Spectros-copy, 1956.

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# **Evaluation of Radiochemical Separation Procedures**

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▶ This four-part paper presents the results of a program of critical evaluation of radiochemical separation procedures for barium, strontium, calcium, and silver. Chromate, nitrate, chloride, oxalate, and sulfate precipitations were studied to determine the conditions for optimim radiochemical separation of these three alkaline earth elements, and procedures for the systematic separation of these ions in tracer solutions are discussed. Two standard and two new methods for the separation of radioactive silver were studied and the efficiency of separation from 13 typical radioactive tracers was compared to facilitate the development of optimum procedures to fit individual requirements for yield and decontamination. One of these procedures, isotopic exchange, is given in more detail in a separate discussion. The method is specific for silver and, with a silver chloride surface, radioactive silver may be separated quantitatively in 15 minutes or less. In radiochemical separations, hydrous oxide precipitations are often used as intermediate steps to scavenge tracer amounts of unwanted elements. The

effectiveness of ferric and lanthanum hydroxides as scavengers on 15 representative radioactive tracers is also presented.

**R**ADIOCHEMICAL separation proce-dures are composed of those chemical separation steps which, when applied to radioactive mixtures, yield a chemical species of sufficient purity to be uniquely counted or detected by the use of existing equipment and pres-ent-day techniques. These procedures may include extraction, precipitation, ion exchange, electrolysis, or volatilization steps. Separation may be required from a large variety of diverse elements, as in the case of fission product analysis, or from, neighboring elements in the periodic table, as in procedures for targets bombarded by low energy (a few million electron volts) nuclear particles. In many cases, interfering activities must be reduced by a factor of 10<sup>4</sup> to 10<sup>8</sup> or more, although the yield of the desired activity need not be quantitative. Furthermore, the nuclear characteristics of the desired isotope are often such that the separation must be rapid.

The general analytical-inorganic literature, while detailed in many cases, is often not directly applicable to radiochemical work, where nonequilibrium conditions are the rule rather than the exception. The conditions chosen for a radiochemical separation are often compromises based on standard analytical methods modified to give maximum separation from undesirable elements even at the cost of a lower yield of the desired constituent.

A program of development and critical evaluation of radiochemical separation procedures has been instituted at the University of Michigan. Certain groups of elements are being studied, procedures previously reported in the literature are being evaluated, and the most promising separation steps of these procedures are being explored in detail to determine optimum conditions for high decontamination and yield.

## BARIUM, STRONTIUM, AND CALCIUM

The high-yield fission products, bar-

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ium and strontium, along with calcium, were the first elements studied. A number of different radiochemical separation procedures have been developed (3, 8, 14, 15, 20) for these elements by modification of standard analytical procedures (7, 11, 19, 34). A survey (26, 29) of the nuclear chemical literature indicates that the separations of primary interest for these elements are precipitations with ammonium dichromate, nitric acid, or hydrochloric acid. Oxalate and sulfate precipitations are also of interest, as they are often the final step in preparing the sample for measurement. Applications of solvent extraction or chelation are not promising, and although good separations have been made by ion exchange, time considerations prevent their general applicability for these elements at the present time. A more detailed discussion of this literature survey and the procedures that follow is given by Sunderman (26).

## APPARATUS, REAGENTS, PROCEDURE

Apparatus. International clinical centrifuge.

Centrifuge cones, borosilicate glass graduated, with cone point, 15 ml.

Test tubes,  $100 \times 15$  mm., glass.

Planchets, 1-inch diameter flat stainless steel.

Geiger tube, halogen quenched, 1.4 mg. per sq. cm. window [Model D-34, Nuclear Instrument and Chemical Corp.

(Nuclear-Chicago), Chicago, Ill.]. Scaler, Nuclear Chicago Model 163, scale of 128 (used with Geiger tube).

Scintillation well counter, Nuclear Chicago Model DS-3 with 2-inch addi-

tional lead shielding. Scaler, Nuclear Chicago Model 162, scale of 128, used with well counter, modified to count with preset time and preset count and to reset automatically.

Lead housing for Geiger tube (Technical Associates, Glendale, Calif., No. Al-14A).

pH Meter, Beckman Model H.

Reagents. Ammonium dichromate solution, 100 grams of analyzed reagent per liter of water.

Ammonium oxalate, conforming to ACS specifications, saturated solution in water.

Buffer solutions, ACS reagent grade sodium acetate and acetic acid in the following mixtures (9): pH 4, 0.19 mole of salt plus 0.81 mole of acid per liter; pH 5, 0.68 mole of salt plus 0.32 mole of acid per liter; pH 6, 1.00 mole of salt, ammonium hydroxide added to pH 6.

Fuming nitric acid, ACS reagent grade, 90 to 95% HNO<sub>3</sub>. Analyzed by the pycnometer specific gravity method.

Hydrochloric acid-ether reagent. Four volumes of ACS reagent grade hydrochloric acid to 1 volume of ACS reagent grade anhydrous ether (Mallinckrodt).

Hydrogen chloride, dry gas (Matheson), 99.0%.

Sulfuric acid solution, 10 ml. of con-

centrated acid, ACS, reagent grade per 100 ml. of water (about 1.8M).

Carrier solutions, 10 mg. of ion per ml. (Table I).

Radioactive tracer solutions (Table II)

**Procedures.** Put 10 mg. of carrier and tracer of the contaminating ion in a 15-ml. centrifuge cone and take the necessary steps (Table II) to secure exchange. Add 10 mg. of carrier of appropriate alkaline earth elements. (Also add tracer of alkaline earth elements when determining their yield.) Add reagents to obtain conditions for precipitation, add precipitant, and stir thoroughly. Digest for 5 minutes at room temperature with occasional stirring. Centrifuge for 5 minutes at top speed and remove supernatant liquid with a glass suction tube connected to a vacuum flask-and through a trap to a water aspirator. Slurry the precipitate onto a planchet, then dry, mount, and count with Geiger tube; or transfer to glass tube, stopper, and count in the scintillation well counter.

Dichromate Separation. Neutralize excess acid from carrier and tracer solutions with ammonium hydroxide. Mix in 10 ml. of buffer solution of the desired pH. Precipitate with 2 ml. of ammonium dichromate solution.

Nitrate Separation. Add sufficient fuming nitric acid precipitant and water to secure desired concentration of nitric acid (total volume 10 to 15 ml.). After centrifugation, decant supernate to waste storage for nitric acid. (Explosions can occur if this waste is mixed with other wastes containing organic materials.)

Chloride Separations. Procedures A and B. Make up initial solution to either 3 or 1.5 ml. with water. Stir in 10 ml. of hydrochloric acid-ether reagent.

Procedure C. Make up volume of solution to 10 ml. with water.

Procedure D. Make up volume to 8 ml. with water and add 3 ml. of ether.

Procedures C and D. Immerse in ice bath. Bubble in dry hydrogen chloride to saturation (about 1 minute). (When no ether is present, large bubbles of hydrogen chloride come to the surface at saturation. In the presence of ether, the aqueous and organic phases initially present combine into one phase as the solution becomes saturated with hydrogen chloride.)

Oxalate Separation. Dilute initial solution to 8 ml. with water. Add excess of concentrated ammonium hydroxide. (One milliliter is usually satisfactory.) Heat to boiling and stir in 2 ml. of saturated solution of ammonium oxalate. Heat again to boiling and allow to stand while stirring occasionally for 5 minutes without applied heat.

Sulfate Separation. Dilute to 10 ml. with 1M nitric acid. Mix in 1 ml. of 2M sulfuric acid precipitant.

## DISCUSSION

Five different procedures have been studied in detail to determine the

## Table I. Preparation of Carrier Solutions<sup>a</sup>

Carrier		
Ion	Salt Used <sup>5</sup>	$\mathbf{Solvent}$
Ag+	$AgNo_3$	Water
$Ba^{++}$	$\overline{Ba}(NO_3)_2$	Water
Ca++	$Ca(NO_2)_2.4H_2O$	Water
Ce+++	$Ce(NO_3)_3.6H_2O$	Water <sup>c</sup>
Co++	$Co(NO_3)_2$ 6H <sub>2</sub> O	Water
$Cr^{+++}$	$Cr(NO_3)_3.9H_2O$	Water⁰
Cs+	CsCl	Water
I-	NaI	Water
Ir+4	$\mathrm{IrCl}_{4}{}^{d}$	HCl, $0.1M$
Ru+++	$RuCl_3$	HCl, 0.1M
$Se^{+4}$	$H_2SeO_3$	HCl, 1.2M
$Sb^{+++}$	$SbCl_3$	HCl, 3M
$Sn^{++}$	$SnCl_2$ . $2H_2O$	$\mathrm{HCl}^{\acute{e}}$
Sr++	$Sr(NO_3)_2$	Water
Ta +5	$K_2TaF_7$	ſ
Zr +4	$ZrO(NO_3)_2$	$HNO_{3}, 0.5M$
	$2\dot{\mathrm{H}}_{2}\mathrm{O}$	HF, 0.1M

<sup>a</sup> Preparation described in more detail

(26, 29). <sup>b</sup> Reagent grade material used whenever possible

<sup>c</sup> Add HNO<sub>3</sub> to clear if necessary.

<sup>d</sup> Manufacturer's designation was IrCl<sub>3</sub>. Brown color, ready solubility in dilute HCl, and reactions with  $H_2S$  and  $NH_3$ indicated that IrCL was present.

Dissolve in concentrated HCl and dilute with 4 equal volumes of water.

/ Add K<sub>2</sub>TaF<sub>7</sub> to 1 ml. of water containing one drop of concentrated HCl and one drop of 1 to 1 HF; heat to dissolve. Make up fresh immediately before use because of instability.

yields for these elements and the contamination by typical tracer impurities (Tables III and IV).

In radiochemical separations, it is important to know the behavior, under the conditions of the separation, of elements very dissimilar from the desired constituent, as the spectrum of elements present in a radioactive sample may be broad, in some cases including as many as 50 different species. In order to evaluate the potentialities of a given separation procedure thoroughly, decontamination tests were made with tracers of elements representing most of the groups and subgroups of the periodic table. Ten milligrams of inactive carrier of these same elements were used with the tracers for each determination.

Special attention must be paid to the decay schemes and radiations of the tracers, as well as to their chemical characteristics, if the decontamination results are to be reproducible. Nuclear characteristics of these tracers can be found in the literature (12, 26). The scintillation well counter is suitable for measuring most tracers emitting gamma rays or high-energy beta rays, but a thin-window Geiger counter was used for tracers such as calcium-45, strontium-90, and barium-140 emitting weak beta ravs.

Where activities from daughter products interfere in counting, two methods

## Table II. Chemical Characteristics of Tracer Solutions

Isotope <sup>a</sup>	$\begin{array}{c} \text{Received from} \\ \text{ORNL}^b \text{ as} \end{array}$	Diluted with <sup>c</sup>	For Carrier-Tracer Exchange <sup>d</sup>	Used as <sup>e</sup>
1.7 Ag <sup>110</sup>	AgNO3 in HNO3 soln.	$3M \text{ HNO}_3$	Thorough mixing	Ag(I)
2. $Ba^{140}$	BaCl <sub>2</sub> in 0.8M HCl	0.1M HCl	Thorough mixing	Ba(II)
3. $Ca^{45}$	CaCl <sub>2</sub> in HCl soln.	0.1M HCl	Thorough mixing	Ca(II)
4. $Ce^{144}$ Pr <sup>144</sup>	CeCl <sub>3</sub> in HCl soln.	3M HCl	Thorough mixing	Ce(III)
5. $Co^{60}$ 6. $Cr^{51}$ 7. $Cs^{134}$ 8. $I^{131}$	CoCl <sub>2</sub> in HCl soln. CrCl <sub>3</sub> in HCl soln. CsCl in HCl soln. NaI in NaOH, NaHSO <sub>3</sub>	1M HCl 1M HCl 0.1M HCl 0.1M NaOH	Thorough mixing Thorough mixing Thorough mixing Thorough mixing	Co(II) Cr(III) Cs(I) I-
9. Ir <sup>192</sup>	$\operatorname{IrCl}_{6}^{\operatorname{Soll.}}$ in HCl soln.	0.1M HCl	Thorough mixing Ir(IV) carrier in dil. HCl plus tracer	$\mathrm{IrCl}_{6}^{}$
10. $\begin{array}{c} \operatorname{Ru}^{106} \\ \operatorname{Rh}^{106} \end{array}$	RuCl <sub>8</sub> in HCl soln.	Dil. HCl	Thorough mixing Ru(III) carrier in dil. HCl plus tracer	Ru(III)
11. Se <sup>75</sup> 12. Sb <sup>124</sup>	SeCl₄ in HCl soln. SbCl₃ in 3.3M HCl soln.	1 <i>M</i> HCl 3 <i>M</i> HCl	Thorough mixing Sb(III) plus tracer, oxid. to Sb(V) with Br <sub>2</sub> , red. to Sb(III) with hy- draz ne	${ m SeO_3^{}} m Sb(III)$
13. $Sn^{113}$ In <sup>113</sup>	$SnCl_2$ in HCl soln.	5% HCl	SnCl <sub>2</sub> in 5% HCl plus tracer, oxid. in excess NaClO	$\operatorname{Sn}(\mathrm{IV})$
14. Sr <sup>89</sup>	$SrCl_2$ in HCl soln.	Dil. HCl	Thorough mixing	Sr(II)
15. Sr <sup>90</sup> ( Y <sup>90</sup> (	$SrCl_2$ in HCl soln.	Dil. HCl	Thorough mixing	Sr(II)
16. <sup>1</sup> Ta <sup>182</sup>	KTaO₃ in KOH	KOH soln.	Dissolution of car- rier in HCl and HF with warming in presence of tracer <sup>9</sup>	TaF6-
$\left. \begin{array}{c} 17. & \mathrm{Zr}^{95} \\ \mathrm{Nb}^{95} \end{array} \right\}$	Complex in oxalic acid	Dil. oxalic acid	Addition of HF and separation as Ba- $ZrF_6^h$	Zr(IV)

<sup>a</sup> Daughter activities listed with parent.

<sup>b</sup> All radioisotopes used obtained from Isotopes Control Department, Oak Ridge National Laboratories (22).

• To minimize losses from hydrolysis or adsorption, tracers were diluted with solutions a to those in which they were received. Small losses of this type are not generally noticeable, as materials are standardized at each use and small changes are ignored.
 <sup>d</sup> Carrier-tracer exchange required individual attention for each element, especially multiple valence elements and those readily complexed.
 Valence states verified experimentally for all elements having multiple valence states.

Alence states verned experimentally for all elements having multiple valence states. No loss of tracer from solution by hydrolysis or adsorption was observed except Ag<sup>110</sup>, large loss by adsorption on soft glass from dilute acid solution of tracer; no loss from highly acid solution in borosilicate glass. Ta<sup>182</sup>, original ORNL solution showed light brown precipitate containing Ta<sup>182</sup> after standing.

<sup>o</sup> Further evidence for complete carrier-tracer exchange: all tantalum activity in contamination studies accompanied macro amount of tantalum.

In all cases, zirconium tracer was separated from its niobium daughter by precipitation of barium fluozirconate, and zirconium separated from barium by two precipitations of zirconium hydroxide (14).

of measurement are possible. In one, a time lapse of about 10 half lives is allowed between the separation and counting to permit the mixture to reach radioactive equilibrium, where the ratio of parent-to-daughter activity is constant. In the other, the daughter activity is removed prior to the experiment, and the complete separation and measurement are made on the parent activity before the daughter again becomes measurable.

The first method was used in all experiments with the cerium praseodymium, ruthenium-rhodium. and tinindium pairs and in some experiments with the barium-lanthanum and strontium-yttrium couples. Other runs with barium and strontium, and all those with zirconium were made by the second method. Plots of growth and decay curves for these six pairs are available (26, 29).

Chromate. In the classical separa-tion (11) of barium from strontium, barium chromate is precipitated by slow addition of ammonium dichromate to a relatively large volume of hot buffered solution and digested for 1 to 2 hours. Although more alkaline conditions (pH 7 to 8) can be used, a pH of 5 has been suggested for radiochemical work (13).

Precipitations were made from acetate-buffered solutions maintained at pH 4, 5, and 6. Equilibrium is not established, because the precipitation is rapid, the experiment is conducted at room temperature, and only a 5-minute digestion time is allowed; however, quantitative yields are not required. As the pH of this precipitation is raised, the yield of barium increases slightly but the contamination due to strontium increases almost 14-fold. At the same time, the calcium contamination, although still small, is about doubled. Thus, the optimum conditions for the barium chromate separation are those at pH 4.

Table III. Summary of Yield Data of Precipitation Reactions for Barium. Strontium, and Calcium<sup>e</sup>

Precipitating			Per Cent	Carried	
Solution	Condition	Barium	Strontium	Ca on Ba	Ca on Sr
Ammonium dichro- mate	pH 4 pH 5 pH 6	$70 \pm 3.4$ $73 \pm 4.0$ $86 \pm 1.3$	$egin{array}{cccc} 1.6 \pm 0.3 \\ 8 \pm 0.2 \\ 22 \pm 2.0 \end{array}$	$\begin{array}{c} 0.8 \pm 0.08 \\ 1.1 \pm 0.08 \\ 1.7 \pm 0.22 \end{array}$	
Nitric acid	80% 70% 60%	$100 \pm 5.3$ $100 \pm 3.6$ $86 \pm 3.3$	$egin{array}{ccc} 100 & \pm 1.7 \\ 98 & \pm 1.4 \\ 81 & \pm 4.2 \end{array}$	$\begin{array}{c} 27 & \pm 2.2 \\ 2.4 \pm 0.3 \\ 0.9 \pm 0.05 \end{array}$	$51 \pm 3.2 \\ 11 \pm 2.3 \\ 2.6 \pm 1.0$
Hydrochloric acid	A. 3 ml. $H_2O$ B. 1.5 ml. $H_2O$ C. Dry HCl D. Ether-dry HCl	$82 \pm 1.1$ $92 \pm 2.2$ $99 \pm 0.4$ $93 \pm 2.4$	$\begin{array}{c} 2.8 \pm 0.9 \\ 11 \ \pm 0.7 \\ 7.3 \pm 1.6 \\ 6.0 \pm 3 \end{array}$	$\begin{array}{c} 0.6 \pm 0.4 \\ 0.8 \pm 0.08 \\ 1.0 \pm 0.1 \\ 1.5 \pm 0.1 \end{array}$	
Ammonium oxalate	95°	59 on SrC2O4 15 on CaC2O4	99		100
Sulfuric acid	Excess sulfate	100	57 on Ba Very slight alone	10	3.6

<sup>a</sup> All values are average of quadruplicate runs. Errors are "standard deviations."

Interferences were determined by a complete separation of barium carrier from strontium carrier in the presence of each contaminant under these optimum conditions. Most of the interfering elements, such as antimony, cerium, iridium, ruthenium, selenium, tantalum, tin, and zirconium, are easily hydrolyzed. Some separation can be obtained from cerium, ruthenium, tantalum, and zirconium, however, because of the slow precipitation of their hydrous oxides under the separation conditions. The insolubility of the silver chromate accounts for the large interference of silver. Antimony gives a large contamination, due not only to hydrous oxide formation but also to the precipitation of basic salts in the weakly acid solution.

Observations during and following precipitation indicate that antimony, tantalum, and tin form precipitates upon addition of the buffer. This is undoubtedly the hydrous oxide of tin, while antimony probably forms an oxychloride, and tantalum an insoluble oxyfluoride.

This chromate method does not require a high degree of separation from diverse elements, as its applicability is primarily in the separation of barium from strontium. A higher degree of separation from easily hydrolyzed elements can be obtained by strong acid precipitations of the alkaline earth elements by nitric or hydrochloric acid reagents.

Nitrate. The Willard and Goodspeed nitric acid method (34) has been frequently used for the separation of barium and strontium from fission products (8, 14, 20). Three different concentrations of nitric acid (80, 70,and 60%) were used in this study to determine the effect of nitrate concentration on the separation of these two elements from calcium, while two concentrations (80 and 60%) were used in the contamination studies. As the concentration of nitric acid is reduced from 80% to 60%, a better separation from calcium results but the yield of barium and strontium is lowered. A sizable amount of calcium can be carried on barium and strontium nitrate precipitates under certain conditions. Calcium nitrate is soluble, however, when present alone in any of these three concentrations of nitric acid (34).

Of the other contaminants studied, only antimony is a major interference. The antimony solution appeared cloudy after centrifuging, an indication of the presence of a second slowly forming solid phase. Two distinct layers of precipitate were visible at the tip of the centrifuge cone, substantiating this premise.

Chloride. Another method for the separation of barium from strontium, calcium, and other elements is based upon the insolubility of barium chloride in strong hydrochloric acid solutions. Many variations of this method have been used in radiochemical work (4, 5, 20). Two of the techniques most often applied are: use of an etherhydrochloric acid solution as the precipitant, keeping the aqueous volume of the radioisotope mixture very low prior to its addition; and use of dry hydrogen chloride gas bubbled into either an aqueous solution or a mixture of ether and water. The first technique involves the use of a fairly stable reagent which can be kept for several days without discoloration. The latter technique requires the use of the highly corrosive dry hydrogen chloride, and an ice bath to remove the heat of solution of the hydrogen chloride.

Two modifications of each of these two techniques were evaluated. The acid concentration for each method was determined by titration with standard sodium hydroxide and the following results were obtained: Procedure A 7.5M, B 8.5M, C 12.0M, and D 7.3M.

Use of the more complicated and hazardous procedures involving dry hydrogen chloride gas is not warranted by the results given in Table III. In fact, precipitation in the procedures using 3 ml. of water and the hydrochloric acid-ether reagent is slower than that using dry hydrogen chloride, giving better decontamination as shown in the case of strontium. Calcium is not a significant interference under any of the conditions used. Although the yield for this procedure was 10% lower than with 1.5 ml. of aqueous solution, and 17% lower than with dry hydrogen chloride, this small loss is in most cases not restrictive, and this procedure was used for the remaining decontamination studies.

Antimony is again the most prominent interference in the contamination tests. A precipitate of silver chloride forms upon addition of the hydrochloric acid-ether reagent, but it readily dissolves in excess reagent. The method is fast and efficient, and requires no precautions other than those normally used in handling ether. The results are generally better than those of nitrate precipitations, because of the lower viscosity of the supernate, which allows more complete removal by suction tube. The barium chloride precipitate is readily soluble in water, thus facilitating further separations.

**Oxalate.** Strontium and calcium oxalate precipitation was included in these studies because it affords a convenient way of quantitatively reducing these elements to a weighable and reproducible form suitable for counting. Precipitation is complete only when the solution is heated and an excess of ammonia is present.

This method is not designed as a decontamination from barium, but as barium is not completely carried, a separation may be made with careful control of conditions (11). The similarity between the crystalline forms of

Table IV.	Contamination of Alkaline Earth Precipitates by Other Activities <sup>a</sup>
	Precipitating Solution 97 Carried

			Precipitating S	olution, $%$	Carried			
	Chromate	80%	60%		Oxa	late		Ions Always Present
$\operatorname{Element}$	pH 4	HNŎ₃	HŃŎ₃	HCl	$\overline{\mathrm{On}\ \mathrm{SrC_2O_4}}$	On $CaC_2O_4$	$\mathbf{Sulfate}$	in Ppting. Soln.
Antimony	55	47	30	28	44	46	28	NO3 <sup></sup> , Cl <sup></sup>
Barium	70	100	86	82	59	15	100	$NO_3^-$ , Cl-
Calcium	0.8	51 on Sr 27 on Ba	2.6  on  Sr 0.9  on  Ba	0.6	• • •	100	10	NO <sub>3</sub> -, CI-
Cerium	6	3.2	2.5	0.9	98	95	71	$NO_2^{-}$ , $Cl^{-}$
Cesium	3.5	1	2	1	0.8	1.6	2.9	$NO_3^{-1}$ Cl <sup></sup>
Chromium	1.2	1.8	1.0	0.7	89	96	$\overline{0}$	$NO_3^{-1}$ , $Cl^{-1}$
Cobalt	1.1	3	3.5	1	52	$\tilde{21}$	0.5	$NO_3^{-1}$ , $Cl^{-1}$
Iodine	2.0	1.2	0.8	0.9	2.3	5.0	1.5	$NO_3^{-}$
Iridium	27	4.2	0.9	5.4	47	68	11	$NO_3^{-1}$ , C1 <sup>-</sup>
Ruthenium	5	1.5	2.4	<b>2</b>	<b>23</b>	38	$\bar{0}.6$	$NO_3^-$ , $Cl^-$
Selenium	5.7	1.4	1.3	0.9	21	23	1.2	$NO_{3}^{-1}$ , Cl <sup>-</sup>
Silver	89	1.9	1.5	0.8	1, 2	2	14	$NO_3^{-\prime}$
Strontium	1.6	100	81	2.8	99		57	$NO_3^-$ , $Cl^-$
Tantalum	10	1	0.7	0.5	49	24	0.6	NO <sub>3</sub> <sup>-,</sup> Cl <sup>-</sup> , F <sup>-</sup>
$\operatorname{Tin}$	99.5	1	1.2	0.8	73	95	0.5	$NO_3$ - $Cl$ -
Zirconium	6.3	2.6	3.3	$^{2}$	93	88	20	$NO_3^{-1}$ (F <sup>-</sup> )?
<sup>a</sup> Average	of duplicates o	on barium precip	oitates, except whe	re noted,				- / \ /

barium and strontium is undoubtedly the cause of the higher contamination of the strontium precipitate by barium, even though the calcium oxalate is more flocculent.

The other contamination studies show many interferences with both precipitates. With antimony, cerium, tin, and zirconium, addition of the ammonia causes immediate precipitation; coagulation is accelerated by boiling. Iridium and ruthenium are complexed by the addition of ammonia, but the complex is destroyed by boiling and the oxide precipitated. Precipitation of this oxide occurs concurrently with that of the oxalate and thus shows clearly the flocculent character of the calcium oxalate. The coagulation of the oxide precipitate of tantalum and cobalt is visibly more rapid with strontium than with calcium. Selenium begins to precipitate when the ammoniacal solution is heated prior to addition of oxalate.

Sulfate. The precipitation of barium sulfate is not generally used in a separation procedure because of difficulty in performing further operations on this highly insoluble substance. It is most useful as a final step in a procedure to secure a form which can readily be dried, weighed, and mounted for counting.

Conditions for the quantitative precipitation involve the slow addition of dilute sulfuric acid to a hot barium solution, followed by a lengthy digestion period ( $\gamma$ ). In more recent work, the sulfate ion is liberated by the thermal decomposition of dimethyl sulfate, thus accomplishing homogeneous precipitation ( $\beta$ ).

In the present work barium is completely precipitated, while about half of the strontium and only 10% of the calcium are carried on the barium sulfate. Strontium sulfate is more completely precipitated in the presence of barium or calcium than in their absence. For the precipitation of strontium sulfate, a reagent such as alcohol is required to lower the solubility, and coagulation must be accelerated by heat (6).

Because the precipitate of barium sulfate is highly compact, contamination is only 0.5 to 0.6% for certain elements. Those ions carried to a larger extent are carried by other than purely mechanical means. For example, silver sulfate is sparingly soluble in these solutions, as are the oxysulfates of ions such as zirconium(IV) and antimony(III). Insoluble barium salts of the sulfate complexes of zirconium may contribute to its contamination. This may also cause the high cerium contamination.

If it is necessary to work with a barium sulfate precipitate in the course of a separation, it may be dissolved

# RESULTS

The yield and decontamination data presented in Tables III and IV can be used to develop optimum alkaline earth procedures for any type of radioactive mixture. These data were obtained under nonequilibrium conditions and are reproducible only if the conditions described above are closely duplicated.

**Barium.** The primary separation of barium and strontium from other elements is a precipitation of barium and strontium nitrates with 60%nitric acid. This gives an 80% yield for barium and strontium and results in a 50- to 100-fold decrease in contaminants for each cycle. Barium may be separated from strontium either by chromate precipitation at pH 4 or by chloride precipitation with the hydrochloric acid-ether reagent. In either case, the amount of strontium remaining in the precipitate is a factor of 50 below that in the solution. The barium chromate precipitate can be counted directly, although the pH of the precipitation may cause some contamination. The chloride separation is performed in strong acid solution and the general decontamination is better. Final precipitation as the sulfate converts the barium into a form suitable for counting and for determining the yields of the entire procedure. A sample procedure based on these separations is shown in Table V.

Strontium. Strontium is first separated with barium as the nitrate. Barium is then separated by chloride precipitation with the hydrochloric acid-ether reagent in as small a volume as practical. Over 90% of the strontium should remain in the supernate. This precipitation may be repeated to secure a better separation, the amount of barium being reduced by a factor of 10 by each cycle. The supernatant solution containing the strontium is then evaporated or neutralized and the strontium precipitated as oxalate in basic solution.

**Calcium.** This element is also separated as the nitrate with strontium and barium in 80% nitric acid with a



yield of about 70% per cycle. Barium and strontium are then removed by repeated sulfate precipitations in acid solutions. This sulfate separation will remove over 99% of the barium and 60% of the strontium, while removing only 5 to 10% of the calcium per cycle. The supernate is then neutralized and the calcium precipitated as the oxalate.

# SILVER

Silver is of great interest in the atomic energy program, because it is one of the important short-lived fission products (3). Hence, much effort has been expended in characterizing its isotopes and in determining its yield in various nuclear reactions.

Conditions for the quantitative separation of silver have been well defined in standard analytical works (7, 11, 19)and the methods have been well characterized for yields and contamination by foreign material. The literature of radiochemical separations for silver is not so well organized. Some investigators have used silver chloride precipitation cycles or a combination of chloride and sulfide precipitations, while others have made precipitations with sodium hydroxide, iodic acid, hydriodic acid, and benzotriazole. Still other methods include separations by chemical reduction of silver ion to the metal, electrodeposition, ion exchange, and isotopic exchange.

The purpose of this study of silver was not only to choose for evaluation the most popular separation methods but also to explore new methods capable of high decontamination. A more detailed discussion of the literature survey and of the procedures that follow is given by Sunderman (26).

## APPARATUS, REAGENTS, AND PROCEDURES

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

Magnetic stirrer (G. F. Smith Chemi-

cal Co., Columbus, Ohio). Platinum Electrodes, 10 mm. in diameter, 30 mm. high, 52 mesh (Ameri-can Platinum Works, Newark, N. J.).

Other apparatus as for barium, strontium, and calcium.

Reagents. Aerosol, 1% solution in water.

Ammonium hydroxide, concentrated, ACS reagent grade.

Benzotriazole solution, 2.5%. Dissolve 2.5 grams of Eastman reagent No. 2759 in 30 ml. of concentrated reagent grade ammonium hydroxide and dilute to 100 ml. with water.

Hydrochloric acid, concentrated, ACS reagent grade.

Silver plating bath. Mix 7 ml. of solution of 3M reagent grade sodium cyanide in water with 1 ml. of water solution 5M in sodium hydroxide.

Versene solution, 40%. Add to 400

grams of analyzed reagent grade diammonium dihydrogen Versenate (Bersworth Chemical Co.) sufficient concentrated ammonium hydroxide to dissolve the solid and dilute with water to 1 liter.

Carrier and tracer solutions as for barium, strontium, and calcium.

Precipitation Procedures. Place 10 mg. of carrier and tracer for contaminating element in a 15-ml. centrifuge cone and take steps necessary to secure exchange. Add 10 mg. of silver carrier. Add precipitant, stir, and digest at room temperature for 5 minutes. Centrifuge at top speed for 5 minutes. Remove the supernate by suction and transfer the precipitate to a planchet, then dry, mount, and count with Geiger tube, or transfer to a glass culture tube, stopper, and count in the scintillation well counter.

For Silver Chloride. Add 2 drops of 1% aerosol solution with silver carrier. Dilute to 10 ml. with 1M nitric acid and stir in 2 drops of concentrated hydrochloric acid.

For Silver Benzotriazole, Dilute original solution to 5 ml. with water and stir in 5 ml. of the Versene solution. Add 1 ml. of 2.5% benzotriazole solution as precipitant.

Electrolytic Procedure. Use a test tube 8 cm. high and 15 mm. in diameter for tracer solution. When macro amounts of the contaminating elements are soluble in the plating solution, make the determinations twice, first with 10 mg. of carrier and then without added carrier. When macro amounts of the contaminants are not soluble, use the tracers without added carriers. Add 10 mg. of silver carrier and 8 ml. of cyanide plating solution. Mix thoroughly by magnetic stirring. Connect the circular platinum gauze cathode and platinum wire anode to a source of direct current (battery eliminator) and electrolyze at 4 volts for 15 minutes with rapid stirring. The deposition of the silver is quantitative under these conditions. When electrolysis is complete, remove the electrodes and wash the cathode with water from a wash bottle for 1 minute. Dry the cathode with acetone and count in the scintillation well counter.

Isotopic Exchange Procedure. The separation of radioactive silver by bringing the active solution in contact with a platinum gauze upon which a surface of silver chloride has been deposited is described below.

## DISCUSSION AND RESULTS

Two problems are encountered in the radiochemical procedures for silver: separation of silver from other metals, and separation from halides, especially iodine. The four separations studied include two methods designed to fulfill each of these requirements. The precipitations of the chloride and of the benzotriazole compound were studied as possible alternative steps in a cyclic procedure for separating silver from

other metal ions. They readily supplement each other, as the chloride precipitation is carried out in acid solution while the benzotriazole precipitation is made from the ammoniacal solution of this chloride precipitate. On the other hand, separations by electrodeposition and isotopic exchange were especially advantageous for the decontamination of silver from halide activities.

Precipitation of silver by sulfide or hydroxide, and reduction to metallic silver by chemical means, were not investigated, as these methods were insufficiently specific. Steps involving precipitation of the iodide or iodate suffer from the same contaminants as the chloride, and the precipitates are difficult to dissolve, thereby hindering further chemical operations.

Study of the precipitations revealed that much greater decontamination was afforded by dissolution and reprecipitation than by washing the precipitate, although the manipulations for each required a similar period of time. For this reason, the procedures developed do not include washing of precipitates.

The experimental yields for silver and the contamination of 13 typical tracer activities in these four procedures are summarized in Table VI and Figure 1.

Chloride. The conditions reported in the radiochemical literature for this separation are similar to those recommended in the standard analytical references. Precipitations are made in dilute nitric acid solution by the addition of hydrochloric acid, followed by thorough stirring and a period of digestion. When centrifugation is used, heating is not necessary for complete recovery of the precipitate. Addition of the aerosol solution prevents the precipitate from sticking to the sides of the centrifuge cone.

Table VI shows that precipitation of silver chloride is an excellent method of separating silver from many elements. The largest interference is antimony, which is difficult to keep in solution during any change in acidity, particularly when a precipitate is being formed. Iodine is carried quantitatively on the precipitate as the iodide, which, in this case, constitutes the major portion of the precipitate. Other interferences which stand out are those of the platinum group, iridium, and ruthenium. This supports previous observations that multiple chloride precipitations are necessary to separate silver completely from irradiated platinum. Iridium and ruthenium are also significant, though still minor interferences in the separation of silver by isotopic exchange. This may be due to the formation of slightly soluble compounds of silver with the chloride complex of the platinum metals. The presence of zirconium carrier retards the precip-

Table VI. Contamination of Silver Separations<sup>a</sup>

Tracer	Chloride (Carrier Added)	Benzotriazole (Carrier Added)	Electrod Carrier added	leposition No carrier added	Exchange (No Carrier Added)
$\begin{array}{c} Ag^{110b} \\ Ce^{144}, Pr^{144} \\ Co^{60} \\ Cr^{51} \\ Cs^{134} \\ I^{131} \\ Ir^{192} \\ Ru^{106}, Rh^{106} \\ Sb^{124} \\ Se^{75} \\ Sn^{113}, In^{113m} \\ Sr^{90}, Y^{90} \\ Ta^{182} \\ Zr^{96}, Nb^{95} \end{array}$	$\begin{array}{c} 99 \pm 1.3 \\ 0.5 \\ 0.5 \\ 0.5 \\ 0.7 \\ 27 \\ 2.5 \\ 22 \\ 0.5 \\ 0.8 \\ 0.7 \\ 0.6 \\ 0.4 \end{array}$	$\begin{array}{c} 92\pm 5\\ 2.3\\ 2.5\\ 92\\ 2.4\\ 98\\ 29\\ 2.5\\ 52\\ 2.7\\ 77\\ 2.4\\ 87\\ 3.9\end{array}$	$\begin{array}{c} 99 \pm 1.3 \\ \text{Insol.} \\ 0.4 \\ 0.001 \\ 0.2 \\ 0.06 \\ 0.03 \\ 26 \\ 0.04 \\ \text{Insol.} \\ \text{Insol.} \\ \text{Insol.} \\ \text{Insol.} \\ \text{Insol.} \\ \text{Insol.} \end{array}$	$\begin{array}{c} \text{Variable} \\ 24 \\ 0.05 \\ 2.1 \\ 0.004 \\ 0.04 \\ 4-0.2 \\ 0.1 \\ 5 \\ 0.05 \\ 10 \\ 2.5 \\ 6.4 \\ 1.0 \end{array}$	$\begin{array}{c} 99.5 \pm 0.5 \\ 0.0001 \\ 0.001 - 0.0001 \\ 0.001 \\ 0.0001 \\ 0.01 - 0.001 \\ 0.1 - 0.01 \\ 0.1 \\ 0.01 \\ 0.1 \\ 0.001 \\ 0.0001 \\ 0.01 \\ 0.01 \\ 0.01 - 0.001 \end{array}$
• Average of	of duplicate r	uns except for si	lver.		

<sup>b</sup> Average of quadruplicate runs. Errors are "standard deviations."

itation of silver chloride and prevents it from being quantitative.

The precipitation of silver chloride is thus very useful as the first step of a series in the separation of silver. The precipitate may be dissolved in ammonia and reprecipitated by acidification with no loss in yield. It may be dissolved in cyanide and then recovered by electrodeposition, or dissolved in ammonia and then precipitated as the silver-benzotriazole compound.

The minimum contamination of the silver chloride precipitate is of the order of 0.5%. This probably is due to the adherence of the supernate to the sides of the centrifuge cone and its occlusion in the precipitate. This minimum also holds for barium chromate and barium sulfate, two very compact precipitates described above, and may represent the best decontamination possible by rapid precipitation of 10 mg. of a carrier in a volume of 10 to 15 ml.

Benzotriazole. This silver separation was chosen to demonstrate the contamination difficulties involved in relatively bulky organic precipitates. Precipitation of silver with this reagent is satisfactory only in the presence of a large concentration of a complexing agent such as Versene, in ammoniacal solution to prevent the precipitation of many normally insoluble hydrous oxides. Under these conditions, according to Cheng (2), 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.

The lack of quantitative recovery of the silver in this procedure (Table VI) is due primarily to the slowness of precipitation and coagulation in the highly salted solution. The bulky character of the precipitate caused it to adhere to the sides of the cone. Every effort was made, however, to transfer this portion as well as that in the cone tip to the counting sample.

The limit of the specificity of this reaction 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. No detectable chloride ion remains after a precipitation from 0.1M chloride solution and one water wash. The mechanical limit of decontamination appears to be around 2.5%. As little of this is due to increased adherence of the liquid to the sides of the centrifuge cone, it must be considered an occlusion phenomenon. Washing the benzotriazole precipitate reduced the contamination by a factor of 2, while dissolution and reprecipitation reduced it by a factor of 40 for a contaminant such as cesium.

Attempts were made to dissolve the precipitate in an organic solvent, immiscible with water, and thereby to extract the silver. Unfortunately no common solvent was found; those which showed promise were either miscible with water or reacted with it.

Electrolytic. Despite the extensive literature on the separation of silver by electrodeposition, the method has found surprisingly few applications in radiochemical work (10, 24, 33). Some references recommended deposition from acid solution. However, the high current densities required to deposit 10 mg. of silver in 15 minutes from an acid solution resulted in a deposit completely unsuitable for quantitative removal. Thus the solution chosen was that used commercially in the plating industry. It contains sufficient cyanide to hold in solution those elements which complex with cyanide and sufficient base to assure the solubility of amphoteric elements.

This procedure gave quantitative recovery of silver when more than 2.5 mg. of silver were present. With smaller amounts of silver, the yield was reduced by dissolution of some of the silver by the plating bath during removal of the cathode.

Electrodeposition of silver can be used to advantage both in carrier-free solutions of radioactive elements and in solutions with carrier present. Contamination determinations were made both with and without added carrier. In some instances, macro amounts of the contaminants were not soluble in the alkaline cyanide solution. Thus, contaminations for solutions in which no carrier had been added vary from as low as 0.05% for cobalt to 24% for cerium. Macro amounts of antimony caused a competing electrode reaction and resulted in the inclusion of 26% of the antimony present. Where macro amounts of the contaminating elements were soluble, decontamination was satisfactory.

The importance of electrodeposition lies in its usefulness in the separation of silver from halides, particularly iodine. Isotopic exchange gives better





decontamination but requires prior oxidation of the iodide to iodate. When it is necessary to purify silver iodide, the precipitate may be dissolved in the cyanide plating solution and the silver then readily deposited.

Electrodeposition, coupled with isotopic exchange, produces a decontamination of  $10^7$  from iodine in a 30minute procedure. This procedure, shown in Table VII, gives quantitative recovery of silver decontaminated from other activities by factors of from  $10^4$ to  $10^{10}$ .

# SILVER BY ISOTOPIC EXCHANGE

The exchange of silver ion between a precipitate of silver chloride and a solution of silver nitrate reaches isotopic equilibrium very rapidly. Because of the low solubility of silver chloride, a very favorable ratio exists at equilibrium between the silver atoms in the precipitate and in the solution. For this reason, 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 the silver in the precipitate by the time equilibrium is attained. Use has been made of this fact to develop a rapid, high decontamination, single-step method for the separation of traces of radioactive silver from a solution containing other radioactive species.

Greater than 99% recovery of silver should be possible with this procedure, as long as the weight of solid inactive silver chloride is more than 100 times the weight of trace silver in the solution.

By use of isotopic exchange (27, 28), it is possible to shorten existing radiochemical procedures for the separation of silver without sacrificing specificity or yield. Isotopic exchange involving silver halides and silver salts in solution has been studied by Langer (17, 18) and applied by him to the determination of macro amounts of silver (16) by a radiometric method. This technique has also been applied to the preparation of beta-ray sources (21) and the separation of iodine-131 (30). A seemingly similar method (1) for the separation of radioiodide on a column of silver chloride granules is based upon elemental chemical substitution of iodide for chloride in a silver chloride substrate rather than upon exchange of radioiodide ions with a silver iodide substrate.

### APPARATUS AND REAGENTS

Apparatus used was similar to that described above. All nonradioactive chemicals were of c.p. or analyzed reagent grade. Radioactive tracers were used without added stable carrier.

# EXPERIMENTAL PROCEDURE

A "silver chloride electrode" of large



# Table VIII. Contamination of Silver by Other Radioactivities in Isotopic Exchange Method<sup>a</sup>

Redicactivity		% C	arried
reautoactivity		011	Gauze
$Hg^{203}$ ( $Hg_{2}^{++}$ )		7	
$Hg^{203}(Hg^{++})$		4	
Bi <sup>210</sup>		1.6	
Ph <sup>214</sup>	<	03	
Bu 106 Bh 106	-	0 1	
Se75		0 1	
Tr192		$\hat{0}$ $\hat{1}_{-}$	0 01
Sn113 In113		0.1	0.01
$T_{1204}^{(11)}(T_{1}^{(1)}+)$		0 04	0.01
$Cr^{51}$		0.01	
Sh124		0.01	
DD		0.01	
$I_{131}(I_{10} -)$		0.01	0.001
$1^{101}(10_3)$		0.01	-0.001
Zr <sup>50</sup> , ND <sup>55</sup>		0.01	-0.001
Co <sup>™</sup>		0.00	1-0.0001
$Ce^{144}$ , $Pr^{144}$		0.00	01
$Cs^{134}$		0.00	01
Sr <sup>90</sup> , Y <sup>90</sup>		0.00	01
Ba <sup>140</sup> , La <sup>140</sup>		0.00	005
<sup>a</sup> Average of at	least	two	determina-

surface area is made from a platinum electrode of 52-mesh gauze, 10 mm. in diameter and 30 mm. high. The required amount of silver metal is first deposited on the gauze by electrolysis for 10 minutes at 4 volts from 10 ml. of a solution 3M in sodium cyanide and 0.5M in sodium hydroxide. A simple battery eliminator is used as a source of voltage. The whitish surface of silver metal is rinsed with water, and then inserted in 10 ml. of 0.05M hydrochloric acid and electrolyzed as the anode for 5

minutes at 1 volt; this completely con-

verts the silver metal to silver chloride.

The electrode is washed with 8M nitric

acid and is ready for use.

tions

To separate silver by isotopic exchange, the silver chloride electrode is brought in contact with 10 ml. of solution containing a very low concentration of radioactive silver. The solution is stirred magnetically. The gauze is then removed from the solution, washed with 8M nitric acid for 1 minute, rinsed with acetone, and counted in the scintillation well counter. When a more reproduci-ble counting form is desired, the silver chloride may be dissolved from the gauze with a small amount of concentrated ammonium hydroxide. This solution is then diluted to 8 ml. and acidified with concentrated nitric acid and the silver chloride precipitate is separated by centrifugation or filtration and counted.

The standard procedure used for all determinations of silver yield required the use of 10 mg. of silver as silver chloride on the electrode and a 15minute contact period at room temperature with a 1*M* nitric acid solution of the tracer. The silver chloride is then dissolved, transferred to a glass culture tube, reprecipitated, and centrifuged. The supernate is removed and the precipitate counted in the scintillation well counter without removal from the tube. For the decontamination and interference studies it was sufficient to count the gauze directly.

## RESULTS AND DISCUSSION

Yields of Silver. The recovery of silver tracer was studied using 10-, 4-, and 1-mg. amounts of silver as silver chloride on the gauze. Average yield values of  $99.5 \pm 0.5$ ,  $98.9 \pm 0.2$ , and  $94.5 \pm 1.0\%$ , respectively, were found for seven determinations of the 10- and 4-mg., and five of the 1-mg.

samples. (Errors are standard deviations.) For each determination an aliquot of 10,000 to 20,000 counts per minute of silver-110 tracer was used. All samples were counted to a probable error of 0.4%.

The silver chloride surface prepared in the manner described above is not ideal from the point of mechanical stability. 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 used routinely. Reproducible results can be obtained with 4-mg. and even 1-mg. amounts of silver, whenever, because of self-absorption or other considerations, a high specific activity is required.

The lower weight limit of silver on the gauze appears to be dependent upon the manipulatory techniques in plating the silver metal. The more uniform (less spotty) the deposit can be made, the more area is available for exchange. In addition, submilligram amounts of silver appear to be dissolved, or lost in some way, from the electrode during removal from the cyanide solution. These problems are illustrated by Figure 2. Silver-110 was used as a tracer to follow the deposition.

A 15-minute contact time under ideal conditions is more than sufficient for complete removal of the radioactive silver from solution, as shown below. Actually at 25° C., 97% of the silver has been removed at the end of 5 minutes, while over 99% is removed in 6 to 7 minutes. This range of 5 to 7 minutes, however, is very sensitive for interfering ions and the effects of nonideal conditions. The 15-minute period was chosen for the standard procedure to minimize the effect of small changes in acidity, stirring, and the character of the silver chloride deposit.

The 1-minute nitric acid wash of thesilver chloride gauze after exchange is necessary where high decontaminations are desired. Washing for a longer period of time has no additional effect. Nitric acid (8M) was an effective wash solution for all the contaminating activities used. If conditions warrant their use, organic wash solutions can be applied.

It was impossible to reproduce results obtained with this procedure to better than 2 to 3% when the silver chloride was counted on the gauze. This probably was due to unevenness in the original silver chloride coating. For better reproducibility it was essential to dissolve the silver chloride and reprecipitate it for counting.

Silver iodide surfaces are also suitable for the exchange separation of tracer silver. The rate of exchange approximates that with silver chloride,



Figure 2. Influence of total amount of silver present on yield of silver deposited electrolytically from cyanide solution

Table	IX.	Effect	of	Interf	erin	ng Sub-
stances	on	Yield	of	Silver	in	Isotopic
Exchange Method						

Species	$\operatorname{Concn.,}_M$	% Yield of Ag <sup>110</sup>
HNO₃	$1 \\ 4 \\ 8 \\ 12 \\ 16$	99 99 93 91 85
HCl	$\begin{array}{c} 0.05 \\ 0.5 \\ 1.0 \\ 3 \\ 6 \end{array}$	98 99 98 89 41
$\rm H_2SO_4$	$\begin{array}{c} 1.5\\ 3\\ 6\end{array}$	97 90 79
HF	$1.1 \\ 3.3 \\ 6.6 \\ 13.2 \\ 22$	98 98 83 57 18
$\mathrm{HC}_{2}\mathrm{H}_{3}\mathrm{O}_{2}$	99%	42
$Al(NO_3)_3$	$egin{array}{c} 0.5 \ 1 \ 2 \end{array}$	99 95 86
$\mathrm{Cu}(\mathrm{NO}_3)_2$	$egin{array}{c} 0.5 \ 1 \ 2 \end{array}$	98 97 95
${\rm Zn}({\rm NO}_3)_2$	$1 \\ 2$	97 95
$Fe(NO_3)_3$	$egin{array}{c} 0.5 \ 1 \ 2 \end{array}$	95 93 94
${ m Bi(NO_3)_3}$	$egin{array}{c} 0.5 \ 1 \ 2 \end{array}$	$100 \\ 97 \\ 93$
$\rm NaC_2H_3O_2$	$egin{array}{c} 0.5 \ 1 \ 2 \end{array}$	98 97 95
$C_2H_5OH$	$25\% \\ 50 \\ 99$	98 95 36
$(\mathrm{CH}_3)_2\mathrm{CO}$	$25\% \\ 50 \\ 99$	98 95 70

as 97% is removed in 6 minutes and 99% in 9 minutes with 10 mg. of silver as silver iodide. In some cases, the use of iodide may even be advantageous because of its lower solubility, but further separation steps are often complicated by the presence of the radioactive silver on the gauze in the form of the difficultly soluble iodide. These difficulties can be bypassed by electrolyzing the silver iodide gauze (cathode) in a neutral conducting solution such as sodium acetate for 1 minute at a voltage sufficient to decompose the silver iodide. The free silver remaining as a black deposit on the electrode is then dissolved in nitric acid.

**Contamination.** Tracers of more than 20 representative elements were used to test this procedure (Table VIII). Long-lived daughter activities of the tracers were tested with the parent, as no attempt was made to separate parents from daughters. In these experiments the only radioactivity present was that of the contaminant(s) being studied; no carriers were added. The data have been arranged according to decreasing contamination for interpretation of the mechanism of the contamination.

It is remarkable that of the elements tested only mercury and bismuth appear to contaminate the silver gauze to an amount greater than a few parts per thousand. Elements which do show some tendency to contaminate, in general, form very strong halide complexes or insoluble compounds with chloride.

About 10% of tracer iodide is carried on a silver chloride gauze after a 15minute contact. The 0.01% figure for iodine in Table VIII is obtained after the iodine-131 solution has been warmed with 0.5 ml. of concentrated nitric acid and 0.5 ml. of 1M potassium permanganate solution to oxidize the iodide to iodate. The iodate, being more soluble than the chloride by a factor of 100, would not be expected to replace it on the gauze surface.

Thallium, lead, and mercury form relatively insoluble halides much like silver. Because solubilities for thallous chloride, lead chloride, and mercuric chloride are factors of 10², 3  $\times$ 10<sup>2</sup>, and 10<sup>3</sup> greater, respectively, than the solubility of silver iodate, they would not be expected to contaminate to any extent. Mercurous ion on the other hand should interfere about as much as iodide ion if the procedure were run on an untreated solution. Oxidation with the permanganatenitric acid mixture, however, will convert all the mercurous ion to mercuric ion, which should not contaminate.

Table VIII shows that thallous and mercurous ions behave as expected. The lead determinations were made with lead-214 tracer separated from radium solutions and represent only an upper limit on the lead contamination because of difficulties in preparing and assaying the tracer independent from its bismuth daughter. Any significant lead contamination may represent adsorption on the halide at 1M acid similar to that reported by Fajans and Erdey-Grúz as well as Imre ( $\beta 1$ ) at very low acid concentrations.

The mercuric and bismuth ions give very surprising results. The mercury values represent an average of seven determinations for each oxidation state, with several oxidizing and reducing agents. It appears that an insoluble double chloride  $(Ag_2HgCl_4)$ similar to the double iodide  $(Ag_2HgCl_4)$ discussed by Wells (32) may be formed on the gauze. Such a double compound may also explain the high contamination of bismuth ions.

The contamination of the gauze by the complex formers may be by adsorption of chloride complexes of the individual elements on the silver chloride surface. Perhaps these complexes actually replace the silver chloride with insoluble compounds of the type  $Ag_2IrCl_6$ , similar to the slightly soluble  $Cs_2PtCl_6$  or even  $Ag_4Fe(CN)_6$ . If this explanation were true, a less soluble surface such as silver bromide should reduce contamination by these elements and a silver iodide surface should reduce it even further. Experimental studies of ruthenium-rhodium contamination showed 0.1, 0.04, and 0.003%of the tracer carried on silver chloride, bromide, and iodide surfaces, respectively. This indicates that the availability of silver or halide ions, or both, influences the decontamination from this particular activity.

In the cases of zirconium-niobium and tantalum activities, the contamination is probably due to hydrolytic effects such as radiocolloid formation or adsorption of basic salts.

Three additional general determinations of decontamination were made.

First, the silver chloride gauze was brought in contact with a solution containing 4-year-old fission products in unseparated form. After a 15-minute contact, only 0.001% of the fission product activity was found on the gauze.

In the second determination, cadmium metal was bombarded with deuterons in the University of Michigan cyclotron, the target was dissolved in nitric and hydrofluoric acids, and the silver produced by the (d, alpha)reaction was removed at an elevated temperature by isotopic exchange. Because of the rapidity of the exchange separation it was possible to detect a 2-minute silver radioisotope, which was never seen when precipitation separations were used. The decay was followed with the scintillation well counter as well as with a  $4\pi$  beta proportional counter; the decay curves showed as clean a separation from cadmium and indium activities as had been obtained previously from a series of precipitation separations requiring 45 minutes.

For the third determination, a palladium-109 irradiated unit containing about 300 millicuries of the 13-hour palladium activity and 2 to 3 millicuries of silver-111 with a 7.5-day half life was obtained from Oak Ridge National Laboratory. The palladium was dissolved in concentrated nitric acid containing a small amount of hydrochloric acid. This solution was diluted until the nitric acid concentration was 4Mand the palladium concentration less than  $0.5\hat{M}$  and the silver was removed by isotopic exchange. The silver chloride obtained weighed 10 mg. and contained 2 millicuries of silver-111 which gave a reading of 3 roentgens per hour at 6 inches when monitored. Its decay was followed in the scintillation well counter and an end-window Geiger counter. A semilog plot of the decay was linear over more than 5 half lives and no other activity was detected.

Interferences. A study was made of the effects on the separation of inactive chemical species present in varying concentrations and forms in the solution from which tracer silver was to be removed. About 20,000 counts per minute of silver-110 were added to solutions containing a given concentration of interfering species, and the yield of silver was determined by the standard procedure. In these experiments the silver chloride was counted on the gauze with a resulting error of  $\pm 2$  to 3%, as explained earlier. The species chosen were those with the greatest likelihood of appearance in process and bombardment solutions. The values for the silver tracer yield in these experiments are given in Table IX.

This study of the effect of inactive species in high concentrations revealed few specific interferences. The only substance showing adverse effect at low concentrations was ferric nitrate. Yield values remained between 93 and 95% for this compound. For other salts and acids included in this study, the effect seems to be one of total ion concentration rather than one due to any individual ion.

In Table X the anionic molarity of each salt is listed opposite the concentration at which that salt first caused less than 97% yield of the tracer silver. It would appear that a concentration of anion of greater than 2 to 8M, depending upon whether it is nitrate, chloride, sulfate, fluoride, or acetate, will result in losses of silver under the procedure used. Silver chloride, as freshly precipitated, is well known for its ability to adsorb either positively or negatively charged ions, depending upon which is in excess as in Fajans' adsorption indicator method. To effect isotopic exchange, high ionic Table IX. Interference Summary, Isotopic Exchange Method

Noropic =nene	
Species	Anionic Molarity at First Loss in Yield of Silver
$\begin{array}{c} HNO_{3} \\ HCl \\ H_{2}SO_{4} \\ HF \\ Al(NO_{3})_{3} \\ Bi(NO_{3})_{3} \\ Cu(NO_{3})_{2} \\ Zn(NO_{3})_{2} \\ NaC_{2}H_{3}O_{2} \end{array}$	$\begin{array}{c} 4-8\\ 1-3\\ 1.5-3\\ 3-6\\ 3\\ 3-6\\ 4\\ 4\\ 2\end{array}$

mobility is required in the immediate vicinity of the silver chloride surface. A stable ionic layer adjacent to the exchanging surface might lower this mobility, with resultant loss of yield. Cognizance should be taken of this possibility before this method is adopted for highly salted solutions.

From the two aqueous-organic systems studied it appears that low concentrations of either acetone or ethyl alcohol will not prevent quantitative removal of silver tracer, as they apparently have no specific deactivating effect on the silver chloride surface. The silver chloride gauze did, however, show lower activity toward exchange if it had been previously rinsed with acetone and dried.

Dependence of Yield on Time and Temperature. Shorter contact periods can be used when necessary. Experimental determinations of the extent of exchange for a number of temperatures have been made by Olcott (23) and are plotted against contact time in Figure 3. As would be expected, the exchange is more rapid at the higher temperatures.

Considerable time economies can be realized by raising the temperature of the contacting solution. At 96° C., for example, over 95% of the tracer can be separated with only a 2-minute contact, the 50% point being reached in 20 seconds. Use can be made of this fact to separate short-lived silver radio-isotopes.

Aging of Silver Chloride. The silver chloride gauzes used in most of the work described above were prepared within 1 hour of use. Because of the light sensitivity of silver chloride and the fact that isotopic exchange must necessarily occur on the surface of the electrode, time studies were made of the stability of the silver chloride surface. Gauzes containing 10 mg. of silver as silver chloride were stored in 8M nitric acid for periods up to 1 week, and then used for a silver separation. Exchange yields of  $99.2 \pm 0.8\%$  indicated no adverse effect during 1 weeks' aging. The only light incident upon the gauzes during this period was from

two 100-watt fluorescent tubes about 4 feet above them.

# IRON AND LANTHANUM HYDROX-IDES AS SCAVENGERS

Scavenging involves formation of a bulky precipitate to remove indiscriminately from solution by coprecipitation and adsorption as many active contaminants as possible. The scavenging element may already be present as one of the contaminating activities or it may be a completely different element. Unfortunately, while removing interfering elements, a scavenging precipitate also removes a portion of the desired constituent-thus limiting its applicability in quantitative analytical work. It has, however, been widely used (3, 14, 15, 20, 26) in radiochemical procedures where 100% yield is not required.

Two methods of scavenging have received more attention than others: precipitation of hydrous oxides of elements such as iron or lanthanum, and precipitation of insoluble sulfides of elements such as mercury or tin. The former method is most applicable to the purification of the alkaline earth metals and silver; iron is used as a nonselective scavenging agent, and lanthanum, to remove rare earth activities. Aluminum and cerium(III) are also of interest, but the character of the precipitate and the pH of precipitation make them similar to iron and lanthanum, respectively.

## PROCEDURE

Add 10 mg. of carrier (when used) and tracer of the element under study to a 15-ml. centrifuge cone and take the necessary steps to secure exchange. Increase the volume to 9 ml. with distilled water and add 10 mg. of ferric or lanthanum carrier. Stir in 1 ml. of concentrated ammonium hydroxide. Digest for 5 minutes at top speed and remove the supernate with glass suction tube. Transfer the precipitate to a culture tube, stopper, and count in a scintillation well counter. When the precipitate carries a major portion of the activity, a more accurate count can be made on 1 ml. of the supernate.

For zirconium-niobium use 10 mg. of carrier of each element. For tinindium and strontium-yttrium use 10 mg. of tin and strontium carriers, respectively, and allow sufficient time prior to counting for equilibrium to be attained.

## DISCUSSION AND RESULTS

The chemical properties of iron(III) and lanthanum(III) and the character of the precipitates differ sufficiently to warrant evaluation of each as scavengers. In radiochemical procedures scavenging is used in general only with trace amounts of contaminants. Table XI, however, compares the efficiency of

Table XI. Scavenging by Precipitation of Hydrous Oxides

	% Remaining in Solution <sup>a</sup>					
	Fe(OH)	3 Pptn.	La(OH	) <sub>3</sub> Pptn.		
Element	Carrier present	Carrier absent	Carrier present	Carrier absent		
Antimony Cerium Cesium Chromium Cobalt Indium Iodine Iridium Ruthenium Selenium Silver Strontium	$18 \\ 0.045 \\ 96 \\ 0.30 \\ 83 \\ 0.12 \\ 95.8 \\ 15 \\ 30 \\ 71 \\ 91.3 \\ 96.3$	$\begin{array}{c} 8.1\\ 0.16\\ 92\\ 0.26\\ 23\\ 0.21\\ 92.7\\ 3.9\\ 6.5\\ 36\\ 91.4\\ 11\end{array}$	$\begin{array}{c} 0.9\\ 0.11\\ 97.8\\ 0.46\\ 89\\ 0.14\\ 86.9\\ 4.4\\ 2.7\\ 9 \ (var.)\\ 97.3\\ 85\end{array}$	$\begin{array}{c} 0.8\\ 2.4\\ 97.7\\ 0.23\\ 79\\ 0.20\\ 75\\ 1.0\\ 1.4\\ 11 \ (var.)\\ 96.5\\ 85 \end{array}$		
Tantalum Tin Zirconium-niobium	${ \begin{smallmatrix} 0.03 \\ 1.7 \\ 0.02 \end{smallmatrix} }$	$   \begin{array}{c}     0.08 \\     0.3 \\     0.14   \end{array} $	$\begin{array}{c} 0.3 \\ 0.12 \\ 0.04 \end{array}$	$0.1 \\ 0.19 \\ 4.9$		

<sup>a</sup> Average of duplicate determinations.



Figure 3. Temperature dependence of exchange of silver ion with silver chloride

scavenging in the presence and absence of macro amounts of the contaminating elements. The second series involves the use of carrier-free activities in some cases and in others the use of material of high specific activity (26).

From literature references (26) it appears that lanthanum hydroxide has been used interchangeably with ferric hydroxide for scavenging purposes, although there are marked differences between the two. Ferric hydroxide formed simply by the addition of ammonium hydroxide to an acid solution containing ferric ion is a good scavenger because of its lack of specificity, its rapid coagulation, and its gelatinous nature. The precipitate is first formed in a slightly acid solution (about pH 3), thereby presenting a ready-formed surface for adsorption of ions that precipitate in less acid solutions. On the other hand, lanthanum hydroxide is formed at pH 7 to 8. The solubility product of many hydrous oxides has already been exceeded before the precipitate begins to form; these particles are thereby allowed to serve as nuclei for the formation of the lanthanum precipitate. This precipitate is slower to coagulate, and less voluminous, being only about one third that of the ferric hydroxide when precipitation is complete.

The contaminants which will be removed most effectively by these elements are those which form hydrous oxides in slightly acid or neutral solution, as shown when the experimental data are rearranged in the form of Table XII. Cerium, tantalum, indium, tin, chromium, zirconium, and niobium are carried to greater than 99% in most cases studied. Elements forming unstable ammonia complexes, such as iridium and ruthenium, are carried to a lesser extent. From this table it appears that while lanthanum hydroxide may be the better scavenger when carriers are present, there is little difference between them in the absence of carriers. Iron hydroxide may be less specific in its scavenging action because of its voluminous nature. There seems to be some tendency for iron to scavenge better when no carriers are present, as in the case of antimony, ruthenium, and iridium.

Table XIII compares the ability of the scavenger to leave the desired constituent in solution. The table uses only data obtained with carriers, as results tend to be erratic if carriers are absent. The elements comprising the 80 to 100% group are identical for both scavengers. The specificity of the lanthanum precipitation is again evident, as no elements are found in the 10 to 50% or the 50 to 80% groups.

The value of a given precipitate as a scavenger depends upon its ability to remove a sizable portion of the contaminants while leaving in solution most of the desired constituent. For a scavenging step to warrant inclusion in a separation procedure it must compete with a specific separation step for the desired constituent. Thus to be worth while in procedures for barium or silver, it must remove more than 99% of a number of contaminating activities and allow at least 80% of the desired constituent to remain in solution.

The results summarized in Tables XII and XIII indicate that in the choice of a scavenging agent, as in the choice of a specific separation step for the desired constituent, care must be taken to fit the procedure to the specific separation.

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#### LITERATURE CITED

- (1) Arnott, D. G., Wells-Cole, J., Nature 171, 269 (1953).
- (2) Cheng, K. L., ANAL. CHEM. 26, 1038 (1954).
- (1954).
  (3) Coryell, C. D., Sugarman, N., "Radiochemical Studies. Fission Products," National Nuclear Energy Series IV, Vol. 9, McGraw-Hill, New York, 1951.
  (4) *Ibid.*, p. 1108.
  (5) *Ibid.*, p. 1657.

Table XII. Comparison of Scavengers' Ability to Carry Contaminating Element

Extent of	Elem	nents
Carrying, %	Carrier present	Carrier absent
	Ferric Hydroxide Scavenge	e
9099 9999 . 9	Sn Cr, In	Ir, Sb, Ru Ce, Cr, In, Sn, Zr- Nb
99.9-99.99 Over 99.99	Ce, Ta, Zr-Nb None	Ta None
	Lanthanum Hydroxide Scave	nge
9099 9999.9	Ir, Ru, Se Ce, Cr, In, Sb, Sn, Ta	Ce, Ir, Ru, Zr-Nb Cr, In, Sb, Sn, Ta
99.9-99.99 Over 99.99	Zr-Nb None	None None

Table XIII. Comparison of Scavengers' Ability to Leave Desired Constituent in Solution

Elements Remaining in Solution <sup>a</sup>	
La(OH) <sub>3</sub> pptn.	
None None Ag, Co, Cs, I, Sr	

<sup>a</sup> Carrier present in all cases.

- (6) Elving, P. J., VanAtta, R. E., ANAL. CHEM. 22, 1375 (1950).
   (7) Furman, N. H., "Scott's Standard Methods of Chemical Analysis," Van Nostrand, New York, 1939.
   (8) Garrison, W. M., Hamilton, J. G., U. S. Atomic Energy Commis-sion, Energy Commission, Rept. UCRL-1067 (December 1950).
   (9) Green, A. A., J. Am. Chem. Soc. 55, 2331 (1933)
- 2331 (1933).
- (10) Greiss, J. C., Rogers, L. B., "Study of the Separation of a Tracer of Silver from a Macro Amount of Palla-dium by Electrolysis," U. S. Atomic Energy Commission, Rept. AECD-2299 (June 1948).
  (11) Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., Hoffman, J. I., "Applied Inorganic Analysis," 2nd ed., Wiley, New York, 1953.
  (12) Hollander, J. M., Perlman, I., Seaborg, G. T., Revs. Modern Phys. 25, 469 (1953).
  (13) Hume, D. N., Ballou, N. E., Glen-denin, L. E., U. S. Atomic Energy Commission, Rept. CN-2815 the Separation of a Tracer of Silver

- Commission, Rept. CN-2815 (1945).
- (14) Kleinberg, J., et al., Ibid., LA-1721 (September 1954).
  (15) Klemm, W., FIAT "Review of German Science 1939–1946," Inorganic Chemistry, Part 1, pp. 91–112, Dieteriche'sche Verlagsbuch bendlung Wiesbeden German buch handlung, Wiesbaden, Ger-
- many, 1948. (16) Langer, A., ANAL. CHEM. 22, 1288 (1950).
- (17) Langer, A., J. Chem. Phys. 10, 321 (1942).
- (18) *Ibid.*, **11**, 11 (1943).
- (18) Iota., 11, 11 (1945).
  (19) McAlpine, R. K., Soule, B. A., "Prescott and Johnson's Quali-tative Chemical Analysis," Van Nostrand, New York, 1933.
  (20) Meinke, W. W., U. S. Atomic Energy Commission, Repts. AFCD 2728. AFCD 2750. (August.)
- AECD-2738, AECD-2750 (August 1949).
- (21) Meinke, W. W., Sunderman, D. N., Nucleonics 13, No. 12, 58 (1955).

- (22) Oak Ridge National Laboratory, (22) Oak Ridge National Laboratory, U. S. Atomic Energy Commission, Carbide and Carbon Chemicals Co., P. O. Box E, Oak Ridge, Tenn., "Isotopes, Radioactive and Stable," Catalog, 1955.
  (23) Olcott, T. W., U. S. Atomic Energy Commission, Rept. AECU-3372 (October 1956)
- (23) Offour, 1. W., O' S. Atomic Energy Commission, Rept. AECU-3372 (October 1956).
   (24) Preiswerk, P., Scherrer, P., Helv. Phys. Acta 20, 153 (1947).

- (25) Pribil, R., Marcova, D., Chem. Listy 45, 542 (1951).
  (26) Sunderman, D. N., Ph.D. thesis, University of Michigan, Febru-ary, 1956 (unpublished); U. S. Atomic Encourt Commission Pant
- ary, 1956 (unpublished); U. S. Atomic Energy Commission, Rept. AECU-3159.
  (27) Sunderman, D. N., Meinke, W. W., Science 121, 777 (1955).
  (28) Sunderman, D. N., Meinke, W. W., U. S. Atomic Energy Commission, Rept. AECU-2988 (January 1955).
  (29) Ibid., Rept. AECU-3360 (1955).
  (30) Sunderman, D. N., Meinke, W. W., "Utilization of Isotopic Exchange for Badochemical Senarations."
- for Radiochemical Separations." Nuclear Engineering and Science Congress, Cleveland, Ohio, De-cember 14, 1955.
  (31) Wahl, A. C., Bonner, N. A., "Radio-activity Applied to Chemistry," p. 128, Wiley, New York, 1951.
  (32) Wells, A. F., "Structural Inorganic Chemistry," p. 164, Clarendon Press, Oxford, 1945.
  (33) Wilkinson, G., Grummitt, W. E., Nucleonics 9, No. 3, 52 (1951).
  (34) Willard, H. H., Goodspeed, E. W. IND. ENG. CHEM., ANAL. ED., 8, 414 (1936). for Radiochemical Separations.

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