

# 14 SEPARATION TECHNIQUES

## 14.1 Introduction

The methods for separation, collection, and detection of radionuclides are similar to ordinary analytical procedures and employ many of the chemical and physical principles that apply to their nonradioactive isotopes. However, some important aspects of the behavior of radionuclides are significantly different, resulting in challenges to the radiochemist to find a means for isolation of a pure sample for analysis (Friedlander et al., 1981, pp. 292-293).

The contents of Chapter 14 provide in one reference document: (1) a review of the important chemical principles that constitute the foundation of radiochemical separations, (2) a survey of the important separation methods used in radiochemistry with a discussion of the advantages and disadvantages of each method, and (3) an examination of the particular features of radioanalytical chemistry that differentiate it from ordinary analytical chemistry. Extensive examples have been employed throughout the chapter to illustrate various principles, practices, and procedures in radiochemistry. Many were purposely selected from agency procedural manuals to provide illustrations from familiar and available documents. Others were taken from the classical and recent radiochemical literature to afford a broad, general overview of the subject.

The material in this chapter is presented in three topic areas. It begins with a review of oxidation-reduction processes and complex-ion formation, two subjects that constitute the principal foundation of radiochemistry procedures and provide background for the topics to follow. The chapter continues with a description of separation techniques commonly found in radiochemical procedures: solvent extraction, volatilization and distillation, electrodeposition, chromatography, and precipitation and coprecipitation. It concludes with two subjects unique to radioanalytical chemistry: carriers and tracers, and radiochemical equilibrium. This organization is designed to provide a developmental approach to the description of each topic area. Explanation of the separation techniques, for example, is dependent on basic chemical principles generally known to the reader, as well as the specific principles developed in the preceding sections. Descriptions of carriers and tracers, and radiochemical equilibrium are contingent on an adequate knowledge of preceding topics, and their explanation makes extensive use of the principles developed in these sections. In all sections of Chapter 14, specific radionuclide examples are used to illustrate the principles and practices involved. Practical guidance is also provided for the practicing radiochemist.

Because the radiochemist detects atoms by their radiation, the success or failure of a radiochemical procedure often depends on the ability to separate extremely small quantities of radionuclides (e.g.,  $10^{-6}$  to  $10^{-12}$  g) that might interfere with detection of the analyte. For example,

35 isolation of trace quantities of a radionuclide that will not precipitate on their own with a counter-  
36 ion requires judicious selection of a carrier and careful technique to produce a coprecipitate  
37 containing the pure radionuclide, free of interfering ions. In detection procedures, the differences  
38 in the behavior of radionuclides provide unique opportunities not available in the traditional  
39 analytical chemistry of nonradioactive elements. Radionuclides can often be detected by their  
40 unique radiation regardless of the chemical form of the element. There is also a time factor  
41 involved, because of the short half-lives of some radionuclides. Traditional procedures involving  
42 long digestions or slow filtrations cannot be used for short-lived radionuclides, thereby requiring  
43 that rapid separations be developed. Another distinction is the hazards associated with  
44 radioactive materials. At very high activity levels (radiolysis), chemical effects of the radiation,  
45 such as decomposition of solvents and heat effects, can affect the procedures. Equally important,  
46 even at lower activity levels, is the radiation dose (especially with gamma-emitters) that the  
47 radiochemist can receive unless protected by shielding or distance. Even at levels where the  
48 health concerns are minimal, special care needs to be taken to guard against laboratory and  
49 equipment contamination. Moreover, the modern radiochemist should be concerned about the  
50 type and quantity of the waste generated by the chemical procedures employed, because the costs  
51 and difficulties associated with the disposal of low-level and mixed radioactive waste continue to  
52 rise. A review of the basic chemical principles that apply to the analysis of radionuclides is  
53 presented in this chapter with an emphasis on the unique behavior of radionuclides.

## 54 **14.2 Oxidation/Reduction Processes**

### 55 **14.2.1 Introduction**

56 Oxidation and reduction (redox) processes play an important role in radioanalytical chemistry,  
57 particularly from the standpoint of the dissolution, separation, and detection of analytes, tracers,  
58 and carriers. Ion exchange, solvent extraction, and solid-phase extraction separation techniques,  
59 for example, are highly dependent upon the oxidation state of the analytes. Moreover, most  
60 radiochemical procedures involve the addition of a carrier or isotope tracer, and to achieve  
61 quantitative yields, there should be complete equilibration (isotopic exchange) between the added  
62 isotope(s) and all the analyte species present. The oxidation number of a radionuclide can affect  
63 its (1) chemical stability in the presence of water, oxygen, and other natural substances in  
64 solution; (2) reactivity with reagents used in the radioanalytical procedure; (3) solubility in the  
65 presence of other ions and molecules; and (4) behavior in the presence of carriers and tracers.  
66 The oxidation numbers of radionuclides in solution and their susceptibility to change, because of  
67 natural or induced redox processes, are critical, therefore, to the physical and chemical behavior  
68 of radionuclides during these analytical procedures. The differences in mass number of all

69 radionuclides of an element are so small that elements with the same oxidation number will  
70 exhibit the same chemical behavior during radiochemical analysis.

### 71 14.2.2 Oxidation-Reduction Reactions

72 An *oxidation-reduction reaction (redox reaction)* is a reaction in which electrons are  
73 redistributed among the atoms, molecules, or ions in the reaction. In some redox reactions,  
74 electrons are actually transferred from one reacting species to another. *Oxidation* under these  
75 conditions is defined as the loss of electron(s) by an atom or other chemical species, whereas  
76 *reduction* is the gain of electron(s). Two examples will illustrate this type of redox reaction:



79 In the first reaction, uranium (U) loses electrons, becoming a cation, and fluorine (F) gains an  
80 electron, becoming an anion. In the second reaction, the reactants are already ions, but the  
81 plutonium cation ( $\text{Pu}^{+4}$ ) gains electrons, becoming  $\text{Pu}^{+3}$ , and the ferrous ion ( $\text{Fe}^{+2}$ ) loses electrons,  
82 becoming  $\text{Fe}^{+3}$ .

83 In other redox reactions, electrons are not completely transferred from one reacting species to  
84 another: the *electron density* about an atom decreases, while it increases about another atom. The  
85 change in electron density occurs as covalent bonds, in which electrons are shared between two  
86 atoms, are broken, and/or are made during a chemical reaction. In covalent bonds between two  
87 atoms of different elements, one atom is more *electronegative* than the other atom. Electronega-  
88 tivity is the ability of an atom to attract electrons in a covalent bond. One atom, therefore, attracts  
89 the shared pair of electrons more effectively, causing a difference in electron density about the  
90 atoms in the bond. An atom that ends up bonded to a more electronegative atom at the end of a  
91 chemical reaction loses net electron density. Conversely, an atom that ends up bonded to a less  
92 electronegative atom gains net electron density. Electrons are not transferred completely to other  
93 atoms, and ions are not formed because the electrons are still shared between the atoms in the  
94 covalent bond. *Oxidation*, in this case, is defined as the loss of electron density, and *reduction* is  
95 defined as the gain of electron density. When carbon (C) is oxidized to carbon dioxide ( $\text{CO}_2$ ) by  
96 oxygen ( $\text{O}_2$ ):



98 the electron density associated with the carbon atom decreases, and that of the oxygen atoms  
99 increases, because the electronegativity of oxygen is greater than the electronegativity of carbon.  
100 In this example, carbon is oxidized and oxygen is reduced. Another example from the chemistry  
101 of the preparation of gaseous uranium hexafluoride (UF<sub>6</sub>) illustrates this type of redox reaction:



103 Because the order of electronegativity of the atoms increases in the order U<H<F, the uranium  
104 atom in uranium tetrafluoride (UF<sub>4</sub>) is oxidized further as more electronegative fluorine atoms  
105 are added to the metal and shift the electron density away from uranium. Chlorine atoms break  
106 their bonds with fluorine and gain electron density (are reduced) as they bond with each other  
107 instead of the more electronegative fluorine atoms.

108 In a redox reaction, at least one species is oxidized, and at least one species is reduced  
109 simultaneously; one process cannot occur without the other. The *oxidizing agent* is defined as the  
110 substance that causes oxidation of another species by accepting electron(s) from it or increasing  
111 in electron density; it is thereby reduced itself. *Reducing agents* lose electron(s) or electron  
112 density and are therefore oxidized. In the reduction of Pu<sup>+4</sup> to Pu<sup>+3</sup> by the ferrous ion, Fe<sup>+2</sup>, the  
113 reducing agent donates an electron to Pu<sup>+4</sup> and is itself oxidized, while Pu<sup>+4</sup>, the oxidizing agent,  
114 accepts an electron from Fe<sup>+2</sup> and is reduced. Generally, the nonmetallic elements are strong  
115 oxidizing reagents, and the metals are strong reducing agents.

116 To keep track of electrons in oxidation-reduction reactions, it is useful to assign oxidation  
117 numbers to atoms undergoing the changes. *Oxidation numbers (oxidation states)* are a relative  
118 indication of the electron density associated with an atom of an element. The numbers change  
119 during redox reactions, whether they occur by actual transfer of an electron(s) or by unequal  
120 sharing of electrons in a covalent bond. The number increases as the electron density decreases; it  
121 decreases as the electron density increases. From the standpoint of oxidation numbers and in  
122 more general terms, oxidation is defined as an increase in oxidation number, and reduction is  
123 defined as the decrease in oxidation number. Different sets of rules have been developed to  
124 assign oxidation numbers to monatomic ions and to each individual atom in molecules and ions.  
125 One set of rules is simple and especially easy to use. It can be used to determine the oxidation  
126 number of atoms in many, but not all, chemical species. In this set, the rules for assigning  
127 oxidation numbers are listed in order by priority of application; that is, the rule written first in the  
128 list has priority over the rule below it. The rules are applied in the order in which they come in  
129 the list, starting at the top and proceeding down the list of rules until each atom of each element,  
130 not the element only, in a species has been assigned an oxidation number. Generally, all atoms of  
131 each element in a chemical species will have the same oxidation number in that species. (A

specific exception would be nitrogen in the cation and anion in ammonium nitrate,  $\text{NH}_4\text{NO}_3$ .) It is important to remember that in many cases, oxidation numbers are not actual electrical charges, but only a helpful bookkeeping method for following redox reactions or examining various oxidation states. As we will see below, the oxidation number of atoms in isolated elements and monatomic ions are actually the charge on the chemical species. The priority rules are:

1. The sum of oxidation numbers of all atoms in a chemical species adds up to equal the charge on the species. This is zero for elements and compounds because they are electrically neutral species and are the total charge for a monatomic or polyatomic ion.
2. The alkali metals (the IA elements, Li, Na, K, Rb, Cs, and Fr) have an oxidation number of +1; the alkaline earth metals (the IIA elements, Be, Mg, Ca, Sr, Ba, and Ra) have an oxidation number of +2.
3. Fluorine (F) has an oxidation number of -1; hydrogen (H) has an oxidation number of +1.
4. Oxygen has an oxidation number of -2.
5. The halogens (the VIIA elements, F, Cl, Br, I, and At) have an oxidation number of -1.
6. In binary compounds (compounds containing elements), the oxidation number of the oxygen family of elements (the VIA elements, O, S, Se, Te, and Po) is -2; for the nitrogen family of elements (the VA elements except Bi, N, P, As, and Sb), it is -3.

Applying these rules illustrates their use:

1. The oxidation number of metallic uranium and molecular oxygen is 0. Applying rule one, the charge on elements is 0.
2. The oxidation number of  $\text{Pu}^{+4}$  is +4. Applying rule one again, the charge is +4.
3. The oxidation numbers of carbon and oxygen in  $\text{CO}_2$  are +4 and -2, respectively. Applying rule one, the oxidation numbers of each atom must add up to the charge of 0 because carbon dioxide is a molecule. The next rule that applies is rule four. Therefore, the oxidation number of each oxygen atom is -2. The oxidation number of carbon is determined by  $\text{C} + 2(-2) = 0$ , or +4. Notice that there is no charge on carbon and oxygen in carbon dioxide because the compound is molecular and does not consist of ions.

- 159 4. The oxidation numbers of calcium and hydrogen in calcium hydride ( $\text{CaH}_2$ ) are +2 and -1,  
160 respectively. The compound is neutral, and the application of rule one requires that the  
161 oxidation numbers of all atoms add up to 0. By rule two, the oxidation number of calcium  
162 is +2. Applying rule one, the oxidation number of hydrogen is:  $2\text{H} + 2=0$ , or -1. Notice  
163 that in this example, the oxidation number as predicted by the rules does not agree with  
164 rule three, but the number is determined by rules one and two, which take precedence  
165 over rule three.
- 166 5. The oxidation numbers of uranium and oxygen in the uranyl ion,  $\text{UO}_2^{+2}$ , are +6 and -2,  
167 respectively. Applying rule one, the oxidation numbers of each atom must add up to the  
168 charge of +2. Rule four indicates that the oxygen atoms are -2 each. Applying rule one,  
169 the oxidation number of uranium is  $\text{U} + 2(-2) = +2$ , and uranium is +6. In this example,  
170 the charges on uranium and oxygen are not actually +6 and -2, respectively, because the  
171 polyatomic ion is held together through covalent bonds. The charge on the ion is the  
172 result of a deficiency of two electrons.

173 Oxidation numbers (states) are commonly represented by zero and positive and negative  
174 numbers, such as +4, -2, etc. They are sometimes represented by Roman numerals for metals,  
175 especially the oxidation numbers of atoms participating in covalent bonds of a molecule or those  
176 of polyatomic ions. Uranium in  $\text{UO}_2^{+2}$  can be represented as U(VI) instead of  $\text{U}^{+6}$ , or chromium  
177 in  $\text{CrO}_4^{-2}$  as Cr(VI) rather than  $\text{Cr}^{+6}$ .

### 178 14.2.3 Common Oxidation States

179 Some radionuclides, such as cesium (Cs) and thorium (Th), exist in solution in single oxidation  
180 states, as indicated by their position in the periodic table. Others, such as technetium (Tc) and  
181 uranium (U), can exist in multiple oxidation states. Multiple oxidation states of plutonium (Pu)  
182 are commonly found in the same solution.

183 The oxidation state for any element in its free state (when not combined with any other element,  
184 as in  $\text{Cl}_2$  or Ag metal) is zero. The oxidation state of a monatomic ion is equal to the electrical  
185 charge of that ion. The Group IA elements form ions with a single positive charge ( $\text{Li}^{+1}$ ,  $\text{Na}^{+1}$ ,  
186  $\text{K}^{+1}$ ,  $\text{Rb}^{+1}$ , and  $\text{Cs}^{+1}$ ), whereas the Group IIA elements form +2 ions ( $\text{Be}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$ , and  
187  $\text{Ra}^{+2}$ ). The halogens generally form -1 ions ( $\text{F}^{-1}$ ,  $\text{Br}^{-1}$ ,  $\text{Cl}^{-1}$ , and  $\text{I}^{-1}$ ); however, except for fluorine,  
188 the other halogens form oxygen compounds in which several other oxidation states are present  
189 [ $\text{Cl}(\text{I})$  in  $\text{HClO}$  and  $\text{I}(\text{V})$  in  $\text{HIO}_3$ ]. For example, iodine can exist as  $\text{I}^{-1}$ ,  $\text{I}_2$ ,  $\text{IO}^{-1}$ ,  $\text{IO}_3^{-1}$ , and  $\text{IO}_4^{-1}$ .  
190 Oxygen exhibits a -2 oxidation state except when its bonded to fluorine, where it can be +1 or  
191 +2; in peroxides, where the oxidation state is -1; and in superoxides, where it is  $-1/2$ .

192 Each of the transition metals has at least two stable oxidation states, except for Sc, Y, and La  
193 (Group IIIB), which exhibit only the +3 oxidation state. Generally, negative oxidation states are  
194 not observed for these metallic elements. The large number of oxidation states exhibited by the  
195 transition elements leads to an extensive, often complicated, oxidation-reduction chemistry. For  
196 example, oxidation states from -1 through +7 have been observed for technetium, although the  
197 +7 and +4 are most common (Anders, 1960, p. 4). In an oxidizing environment, Tc exists  
198 predominantly in the heptavalent state as the pertechnetate ion,  $\text{TcO}_4^{-1}$ , which is water soluble,  
199 but which can yield insoluble salts with large cations. Technetium forms volatile heptoxides and  
200 acid-insoluble heptasulfides. Subsequently, pertechnetate is easily lost upon evaporation of acid  
201 solutions unless a reducing agent is present or the evaporation is conducted at low temperatures.  
202 Technetium(VII) can be reduced to lower oxidation states by reducing agents such as bisulfite  
203 ( $\text{HSO}_3^{-1}$ ). This process proceeds through several intermediate steps, some of which are slow;  
204 therefore, unless precautions are taken to maintain technetium in the appropriate oxidation state,  
205 erratic results can be obtained. The +7 and +4 ions behave very differently in solution. For  
206 instance, pertechnetate does not coprecipitate with ferric hydroxide, while Tc(IV) does.

207 The oxidation states of the actinide elements have been comprehensively discussed by Ahrlund  
208 (1986, pp. 1480-1481) and Cotton and Wilkinson (1988, pp. 985-987 and pp. 1000-1014). The  
209 actinides exhibit an unusually broad range of oxidation states, of from +2 to +7 in solution.  
210 Similar to the lanthanides, the most common oxidation state is +3 for actinium (Ac), americium  
211 (Am), and curium (Cm). The +4 state is common for thorium and plutonium, whereas +5 is most  
212 common for protactinium (Pa) and neptunium (Np). The most stable state for uranium is the +6  
213 oxidation state.

214 In compounds of the +3 and +4 oxidation states, the elements are present as simple  $\text{M}^{+3}$  or  $\text{M}^{+4}$   
215 cations; but for higher oxidation states, the most common forms in compounds and in solution  
216 are the oxygenated actinyl ions,  $\text{MO}_2^{+1}$  and  $\text{MO}_2^{+2}$ :

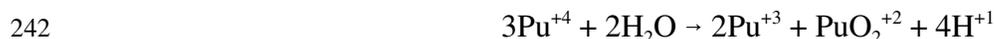
- 217 •  $\text{M}^{+3}$ . The +3 oxidation state is the most stable condition for actinium, americium, and curium.  
218 It is easy to produce  $\text{Pu}^{+3}$ . This stability is of critical importance to the radiochemistry of  
219 plutonium. Many separation schemes take advantage of the fact that Pu can be selectively  
220 maintained in either the +3 or +4 oxidation state. Unlike Pu and Np,  $\text{U}^{+3}$  is such a strong  
221 reducing agent that it is difficult to keep in solution.
- 222 •  $\text{M}^{+4}$ . The only oxidation state of thorium that is experienced in radiochemical separations is  
223 +4.  $\text{Pa}^{+4}$ ,  $\text{U}^{+4}$ , and  $\text{Np}^{+4}$  are stable, but they are easily oxidized by  $\text{O}_2$ . In acid solutions with  
224 low plutonium concentrations,  $\text{Pu}^{+4}$  is stable. Americium and curium can be oxidized to the  
225 +4 state with strong oxidizing agents such as persulfate.

226 • M<sup>+5</sup>. The actinides from protactinium through americium form MO<sub>2</sub><sup>+1</sup> ions in solution. PuO<sub>2</sub><sup>+1</sup>  
 227 can be the dominant species in solution at low concentration in natural waters that are  
 228 relatively free of organic material.

229 • M<sup>+6</sup>. M+6 is the most stable oxidation state of uranium, which exist as the UO<sub>2</sub><sup>+2</sup> species.  
 230 Neptunium, plutonium, and americium also form MO<sub>2</sub><sup>+2</sup> ions in solution. The bond strength,  
 231 as well as the chemical stability toward reduction for these MO<sub>2</sub><sup>+2</sup> ions, decrease in the order  
 232 U > Np > Pu > Am.

233 Reactions that do not involve making or breaking bonds, M<sup>+3</sup> → M<sup>+4</sup> or MO<sub>2</sub><sup>+1</sup> → MO<sub>2</sub><sup>+2</sup>, are fast  
 234 and reversible, while reactions that involve chemical bond formation, M<sup>+3</sup> → MO<sub>2</sub><sup>+1</sup> or  
 235 M<sup>+4</sup> → MO<sub>2</sub><sup>+2</sup>, are slow and irreversible.

236 Plutonium exhibits redox behavior unmatched in the periodic table. It is possible to prepare  
 237 solutions of plutonium ions with appreciable concentrations of four oxidation states, +3, +4, +5,  
 238 and +6, as Pu<sup>+3</sup>, Pu<sup>+4</sup>, PuO<sub>2</sub><sup>+1</sup>, and PuO<sub>2</sub><sup>+2</sup>, respectively. [Detailed discussions can be found in  
 239 Cleveland (1970), Seaborg and Loveland (1990), and in the Coleman (1965) monograph.]  
 240 According to Cleveland (1970), this polyvalent behavior occurs because of the tendency of Pu<sup>+4</sup>  
 241 and Pu<sup>+5</sup> to disproportionate:



244 and because of the slow rates of reaction involving formation or rupture of Pu-O bonds (such as  
 245 PuO<sub>2</sub><sup>+1</sup> and PuO<sub>2</sub><sup>+2</sup>) compared to the much faster reactions involving only electron transfer. The  
 246 distribution depends on the type and concentration of acid used for dissolution, the method of  
 247 solution preparation, and the initial concentration of the different oxidation states. In HCl, HNO<sub>3</sub>,  
 248 and HClO<sub>4</sub>, appreciable concentrations of all four states exist in equilibrium. Seaborg and  
 249 Loveland (1990, p. 88) report that in 0.5 M HCl at 25 °C, the equilibrium percentages of  
 250 plutonium in the various oxidation states are found to be as follows:

251	Pu <sup>+3</sup>	27.2%
252	Pu <sup>+4</sup>	58.4%
253	Pu <sup>+5</sup>	~0.7%
254	Pu <sup>+6</sup>	13.6%

255 Apart from the disproportionation reactions, the oxidation state of plutonium ions in solution is  
 256 affected by its own decay radiation or external gamma and X-rays. Radiolysis products of the  
 257 solution can oxidize or reduce the plutonium, depending on the nature of the solution and the  
 258 oxidation state of plutonium. Therefore, the stated oxidation states of old plutonium solutions,  
 259 particularly old HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> solutions, should be viewed with suspicion. Plutonium also  
 260 tends to hydrolyze and polymerize in solution, further complicating the situation (see Section  
 261 14.10, *Radiochemical Equilibrium*).

262 Tables 14.1 and 14.2 summarize the common oxidation number(s) of some important elements  
 263 encountered in the radioanalytical chemistry of environmental samples and the common  
 264 chemical form of the oxidation state.

265 **TABLE 14.1 — Oxidation states of elements<sup>(1)</sup>**

Element	Oxidation State <sup>(2)</sup>	Chemical Form	Notes
Am	+3 +4 +5 +6	Am <sup>+3</sup> Am <sup>+4</sup> AmO <sub>2</sub> <sup>+1</sup> AmO <sub>2</sub> <sup>+2</sup>	Pink; stable; difficult to oxidize Pink-red; unstable in acid Pink-yellow; disproportionates in strong acid; reduced by products of its own radiation Rum color; stable
Cs	+1	Cs(H <sub>2</sub> O) <sub>x</sub> <sup>+1</sup>	Colorless; x probably is 6
Co	+2 +3	Co(H <sub>2</sub> O) <sub>6</sub> <sup>+2</sup> Co(H <sub>2</sub> O) <sub>6</sub> <sup>+3</sup>	Pink to red; oxidation is very unfavorable in solution Rapidly reduced to +2 by water unless acidic
Fe	+2 +3	Fe(H <sub>2</sub> O) <sub>6</sub> <sup>+2</sup> Fe(H <sub>2</sub> O) <sub>6</sub> <sup>+3</sup>	Green Pale violet; hydrolyses in solution to form yellow or brown complexes
<sup>3</sup> H	+1	<sup>3</sup> HOH and <sup>3</sup> HOH <sub>2</sub> O <sup>+1</sup>	Exchange of tritium is extremely rapid in samples that have water introduced.
I	-1 -1/3 +5 +7	I <sup>-1</sup> I <sub>3</sub> <sup>-1</sup> IO <sub>3</sub> <sup>-1</sup> IO <sub>4</sub> <sup>-1</sup>	Colorless Brown; commonly in solutions of I <sup>-1</sup> exposed to air Colorless; formed in vigorously oxidized solutions Colorless
Ni	+2	Ni(H <sub>2</sub> O) <sub>6</sub> <sup>+2</sup>	Green
Nb	+3 +5	Unknown HNb <sub>6</sub> O <sub>19</sub> <sup>-7</sup>	In sulfuric acid solutions of Nb <sub>2</sub> O <sub>5</sub>
Po	+4		

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Element	Oxidation State <sup>(2)</sup>	Chemical Form	Notes
276 Pu	+3	$\text{Pu}(\text{H}_2\text{O})_x^{+3}$	Violet; stable to air and water; easily oxidized to +4
	<b>+4</b>	$\text{Pu}(\text{H}_2\text{O})_x^{+4}$	Tan; first state formed in freshly prepared solutions; stable in 6 M acid; disproportionates in low acidity to +3 and +6
	+5	$\text{Pu}(\text{H}_2\text{O})_x^{+5}$	Never observed alone; always disproportionates; most stable in low acidity
		or $\text{PuO}_2^{+5}$	Purple
	+6	$\text{PuO}_2^{+5}$	Yellow-pink; stable but fairly easy to reduce
277 Ra	+2	$\text{Ra}(\text{H}_2\text{O})_x^{+2}$	Colorless; behaves chemically like Sr and Ba
		or $\text{PuO}_5^{-3}$	Green
	+7	or $\text{PuO}_4(\text{OH})_2^{-3}$	$\text{PuO}_4(\text{OH})_2^{-3}$ more likely form
278 Sr	+2	$\text{Sr}(\text{H}_2\text{O})_x^{+2}$	Colorless
279 Tc	+4	$\text{TcO}_3^{-2}$	
	+5	$\text{TcO}_3^{-1}$	
	<b>+7</b>	$\text{TcO}_4^{-1}$	
280 Th	+4	$\text{Th}(\text{H}_2\text{O})_8^{+4}$	Colorless; at pH>3 forms complex hydrolysis products
281 U	+3	$\text{U}(\text{H}_2\text{O})_x^{+3}$	Red-brown; slowly oxidized by water and rapidly by air to +4
	<b>+4</b>	$\text{U}(\text{H}_2\text{O})_{8-9}^{+4}$	Green; stable but slowly oxidized by air to +6
	+5	$\text{UO}_2^{+1}$	Unstable but more stable at pH 2-4; disproportionates to +4 and +6
	+6	$\text{UO}_2(\text{H}_2\text{O})_5^{+}$	Yellow; only form stable in solution containing air; difficult to reduce
282 Zr	+4	$\text{Zr}(\text{H}_2\text{O})_6^{+4}$	Only at very low ion concentrations and high acidity
		$\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}^{+2}$	At typical concentrations in absence of complexing agents

- (1) Compiled from: Booman and Rein, 1962; Cotton and Wilkinson, 1988; Emsley, 1989; Greenwood and Earnshaw, 1984; Grinder, 1962; Hampel, 1968; Katzin, 1986; Latimer, 1952; and Pauling, 1970.  
 (2) Most common form is in bold.

TABLE 14.2 — Stable oxidation states of selected elements<sup>(1,2)</sup>

Element	+1	+2	+3	+4	+5	+6	+7	+8
288 Titanium		○	○	●				
289 Vanadium		○	○	●	●			
290 Chromium		●	●	○	○	●		
291 Manganese		●	○	●	○	○	●	
292 Iron		●	●	○		○		
293 Cobalt		●	●					
294 Nickel		●	○	○				
295 Strontium		●						
296 Yttrium			●					
297 Molybdenum		○	○	●	●	●		

Element	+1	+2	+3	+4	+5	+6	+7	+8
298 Technetium		○	○	●	○	○	●	
299 Silver	●		○	○				
300 Cesium	●							
301 Barium		●						
302 Lanthanides			●					
303 Lead		●		○				
304 Polonium		○		●		○		
305 Radium		●						
306 Actinium			●					
307 Thorium				●				
308 Protactinium				○	●			
309 Uranium			○	○	○	●		
310 Neptunium			○	○	●	○	○	
311 Plutonium			○	●	○	○		
312 Americium			●	○	○	○		
313 Curium			●	○				

(1) The stable nonzero oxidation states are indicated. The more common oxidation states are indicated by solid black circles.

(2) Data compiled from Seaborg and Loveland (1990) and the NAS–NRC monographs listed in the references.

#### 14.2.4 Oxidation State in Solution

For the short-lived isotopes that decay by alpha emission or spontaneous fission, high levels of radioactivity cause heating and chemical effects that can alter the nature and behavior of the ions in solution and produce chemical reactions not observed with longer-lived isotopes. Decomposition of water by radiation (*radiolysis*) leads to H and OH free radicals and formation of H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, among other reactive species, and higher oxidation states of plutonium and americium are produced.

The solutions of some ions are also complicated by *disproportionation*, the autooxidation-reduction of a chemical species in a single oxidation state to higher and lower oxidation states. The processes are particularly dependent on the pH of the solution. Oxidation of iodine, uranium, americium, and plutonium are all susceptible to this change in solution. The disproportionation of UO<sub>2</sub><sup>+1</sup>, for example, is represented by the chemical equation:



331 The magnitude of the equilibrium constant reflects the instability of the +5 oxidation state of  
332 uranium in  $\text{UO}_2^{+1}$  described in Table 14.1, and the presence of hydrogen ions reveals the  
333 influence of acidity on the redox process. An increase in acidity promotes the reaction.

#### 334 14.2.5 Common Oxidizing and Reducing Agents

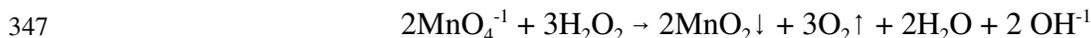
335 HYDROGEN PEROXIDE. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) has many practical applications in the  
336 laboratory. It is a very strong oxidizing agent that will spontaneously oxidize many organic  
337 substances, and water samples are frequently boiled with peroxide to destroy organic compounds  
338 before separation procedures. When hydrogen peroxide serves as an oxidizing reagent, each  
339 oxygen atom changes its oxidation state from -1 to -2. For example, the reaction for the oxidation  
340 of ferrous ion is as follows:



342 Hydrogen peroxide is frequently employed to oxidize  $\text{Tc}^{+4}$  to the pertechnetate:



344 Hydrogen peroxide can also serve as a reducing agent, with an increase in oxidation state from -  
345 1 to 0, and the liberation of molecular oxygen. For example, hydrogen peroxide will reduce  
346 permanganate ion ( $\text{MnO}_4^{-1}$ ) in basic solution, forming a precipitate of manganese dioxide:



348 Furthermore, hydrogen peroxide can decompose by the reaction:



350 This reaction is another example of a disproportionation (autooxidation-reduction) in which a  
351 chemical species acts simultaneously as an oxidizing and reducing agent; half of the oxygen  
352 atoms are reduced to  $\text{O}^{-2}$ , and the other half are oxidized to elemental oxygen ( $\text{O}^0$ ) in the diatomic  
353 state,  $\text{O}_2$ .

354 OXYANIONS. Oxyanions ( $\text{NO}_3^{-1}$ ,  $\text{Cr}_2\text{O}_7^{-2}$ ,  $\text{ClO}_3^{-1}$ , and  $\text{MnO}_4^{-1}$ ) differ greatly in their oxidizing  
355 strength, but they do share certain characteristics. They are stronger oxidizing agents in acidic  
356 rather than basic or neutral conditions, and they can be reduced to a variety of species depending

357 on the experimental conditions. For example, on reduction in acidic solutions, the permanganate  
358 ion accepts five electrons, forming the manganous ion  $Mn^{+2}$ :



360 In neutral or basic solution, permanganate accepts 3 electrons, and forms manganese dioxide  
361 ( $MnO_2$ ), which precipitates:



363 These oxidizing agents are discussed further in Section 12.4, “Wet Ashing and Acid Dissolution  
364 Techniques.”

365 NITRITE. Nitrite ion ( $NO_2^{-1}$ ), plays an important role in the manipulation of Pu oxidation states in  
366 solution. It is capable of oxidizing  $Pu^{+3}$  to  $Pu^{+4}$  and of reducing  $Pu^{+6}$  to  $Pu^{+4}$ . Because most  
367 aqueous processes center around  $Pu^{+4}$ , sodium nitrite ( $NaNO_2$ ) is frequently used as a valence  
368 adjuster to convert all Pu to the +4 state. And because the  $Pu^{+6} \rightarrow Pu^{+4}$  reaction by nitrite is slow,  
369 another reducing agent, such as the ferrous ion, often is added to increase the rate of reaction.

370 PERCHLORIC ACID. The use of perchloric acid ( $HClO_4$ ) as an oxidizing agent is covered in depth  
371 in Section 12.4, “Wet Ashing and Acid Dissolution Techniques.”

372 METALS IONS. Generally, metals ions ( $Ti^{+3}$ ,  $Cr^{+2}$ ,  $Fe^{+2}$ , etc.) are strong reducing agents. For  
373 example, both  $Ti^{+3}$  and  $Cr^{+2}$  have been shown to reduce  $Pu^{+4}$  to  $Pu^{+3}$  rapidly in acidic media.  
374  $Fe^{+2}$  rapidly reduces  $Np^{+5}$  to  $Np^{+4}$  in  $H_2SO_4$ .

375  $Ti^{+3}$  is used extensively as a reducing agent in both inorganic and organic analyses.  $Ti^{+3}$  is  
376 obtained by reducing  $Ti^{+4}$ , either electrolytically or with zinc.  $Ti^{+4}$  is the most stable and common  
377 oxidation state of titanium. Compounds in the lower oxidation states (-1, 0, +2, and +3) are quite  
378 readily oxidized to  $Ti^{+4}$  by air, water, or other reagents.

379 ASCORBIC ACID. Commonly known as vitamin C, ascorbic acid is an important reducing agent  
380 for the radiochemist. Because the ferric ion interferes with the uptake of  $Am^{+3}$  in several popular  
381 extraction schemes, ascorbic acid is frequently used to reduce  $Fe^{+3}$  to  $Fe^{+2}$  to remove this  
382 interference. Ascorbic acid is also used to reduce  $Pu^{+4}$  to  $Pu^{+3}$ .

383 **14.2.6 Oxidation State and Radiochemical Analysis**

384 Most radiochemical analyses require the radionuclide be in aqueous solution. Thus, except for  
 385 water samples, the first step of an analysis is the complete dissolution of the sample so that all  
 386 components remaining at the end of the process are in a true solution. Dissolution of many  
 387 samples requires vigorous conditions to release the radionuclides from its natural matrix. Strong  
 388 mineral acids or strong bases, which also serve as powerful oxidizing agents, are used in boiling  
 389 mixtures or under fusion conditions to decompose the matrix—evaporating portions of the acid  
 390 or base from the mixture and oxidizing the radionuclide to a common oxidation state. The final  
 391 state depends, generally, on the radionuclide, oxidizers used, and pH of the solution (see notes in  
 392 Table 14.1, Section 14.2.3, “Common Oxidation States”). Even water samples might contain  
 393 radionuclides at various states of oxidation because of their exposure to a variety of natural  
 394 oxidizing conditions in the environment and the pH of the sample.

395 Once the analyte is in solution, the radioelement and the tracers and carriers used in the  
 396 procedure must be in the same oxidation state to ensure the same chemical behavior (Section  
 397 14.10.2, “Oxidation State”). For radionuclides that can exist in multiple oxidation states, one  
 398 state must be achieved; for those such as plutonium, which disproportionates, a reproducible  
 399 equilibrium mixture of all oxidation states can be established. Oxidizing or reducing agents are  
 400 added to the reaction mixture to establish the required conditions. Table 14.3 contains a summary  
 401 of several chemical methods for the oxidation and reduction of select radionuclides.

402 **TABLE 14.3 — Redox reagents for radionuclides<sup>(1)</sup>**

Redox Reaction	Reagent	Conditions
Am <sup>+3</sup> → AmO <sub>2</sub> <sup>+2</sup>	Ag <sup>+2</sup> , Ag <sup>+</sup> /S <sub>2</sub> O <sub>8</sub>	
Am <sup>+4</sup> → AmO <sub>2</sub> <sup>+2</sup>	O <sub>3</sub>	13 M NH <sub>4</sub> F
AmO <sub>2</sub> <sup>+1</sup> → AmO <sub>2</sub> <sup>+2</sup>	Ce <sup>+4</sup>	HClO <sub>4</sub>
	O <sub>3</sub>	Heated HNO <sub>3</sub> or HClO <sub>4</sub>
AmO <sub>2</sub> <sup>+2</sup> → AmO <sub>2</sub> <sup>+1</sup>	Br <sup>-1</sup> , Cl <sup>-1</sup>	
	Na <sub>2</sub> CO <sub>3</sub>	Heat to precipitate NaAmO <sub>2</sub> CO <sub>3</sub> ; dissolve in H <sup>+1</sup>
AmO <sub>2</sub> <sup>+2</sup> → Am <sup>+3</sup>	I <sup>-1</sup> , H <sub>2</sub> O <sub>2</sub> , NO <sub>2</sub> <sup>-1</sup> , SO <sub>2</sub>	
Am <sup>+4</sup> → Am <sup>+3</sup>	alpha radiation effects	Spontaneous
Co <sup>+2</sup> → Co <sup>+3</sup>	O <sub>3</sub>	Cold HClO <sub>4</sub>
	O <sub>2</sub> , H <sub>2</sub> O <sub>2</sub>	Complexed cobalt
Co <sup>+3</sup> → Co <sup>+2</sup>	H <sub>2</sub> O	Rapid with evolution of H <sub>2</sub>
Fe <sup>+2</sup> → Fe <sup>+3</sup>	O <sub>2</sub>	Faster in base; slower in neutral and acid solution; decreases with H <sup>+1</sup>
	Ce <sup>+4</sup> , MnO <sub>4</sub> <sup>-1</sup> , NO <sub>3</sub> <sup>-1</sup> , NO <sub>2</sub> <sup>-</sup>	
	H <sub>2</sub> O <sub>2</sub> , S <sub>2</sub> O <sub>8</sub> <sup>-2</sup>	

	Redox Reaction	Reagent	Conditions
413	$\text{Fe}^{+3} \rightarrow \text{Fe}^{+2}$	$\text{Cr}_2\text{O}_7^{-2}$ $\text{H}_2\text{S}, \text{H}_2\text{SO}_3$ Zn, Cd, Al, Ag amalgams $\text{Sn}^{+2}, \text{I}^{-1}, \text{Cu}^{+1}, \text{Ti}^{+3}$ $\text{NH}_2\text{OH}$	HCl or $\text{H}_2\text{SO}_4$ Excess removed by boiling Boiling solution
414	$\text{I}^{-1} \rightarrow \text{I}_2$	$\text{HNO}_2$ ( $\text{NaNO}_2$ in acid) $\text{MnO}_2$ in acid 6M $\text{HNO}_3$ $\text{NaHSO}_3$ or $\text{NaHSO}_3$ in $\text{H}^{+1}$ $\text{Na}_2\text{SO}_3; \text{Na}_2\text{S}_2\text{O}_3$	Does not affect other halides Well suited for lab work
415	$\text{I}^{-1} \rightarrow \text{IO}_3^{-1}$	$\text{KMnO}_4$ 50% $\text{CrO}_3$ in 9M $\text{H}_2\text{SO}_4$	
416	$\text{I}^{-1} \rightarrow \text{IO}_4^{-1}$	$\text{NaClO}$ in base	
417	$\text{IO}_4^{-1} \rightarrow \text{I}_2$	$\text{NH}_2\text{OH}\cdot\text{HCl}$ $\text{H}_2\text{C}_2\text{O}_4$	(9 M $\text{H}_2\text{SO}_4$ )
418	$\text{IO}_4^{-1} \rightarrow \text{I}^{-1}$	$\text{NaHSO}_3$ in acid	
419	$\text{I}_2 \rightarrow \text{I}^{-1}$	$\text{SO}_2; \text{NaHSO}_3$	
420	$\text{Pu}^{+3} \rightarrow \text{Pu}^{+4}$	$\text{BrO}_3^{-1}$ $\text{Ce}^{+4}$ $\text{Cr}_2\text{O}_7^{-2}, \text{IO}_3^{-1}, \text{MnO}_4^{-1}$ $\text{NO}_2^{-1}$ $\text{NO}_3^{-1}$ $\text{HNO}_2$	Dilute $\text{H}^{+1}$ HCl or $\text{H}_2\text{SO}_4$ solution Dilute $\text{H}^{+1}$ $\text{HNO}_3$ $\text{HNO}_3$ or dilute HCl (100°C)
421	$\text{Pu}^{+4} \rightarrow \text{PuO}_2^{+2}$	$\text{NaBiO}_3$ $\text{BrO}_3^{-1}$ $\text{Ce}^{+4}$ $\text{HOCl}$ ( $\text{KClO}$ ) $\text{MnO}_4^{-1}$ $\text{O}_3$ Ag(II) $\text{Cr}_2\text{O}_7^{-2}$ $\text{Cl}_2$ $\text{NO}_3^{-1}$ $\text{Ag}_2\text{O}$ $\text{IO}_3^{-}$	$\text{HNO}_3$ Dilute $\text{HNO}_3$ at 85°C Dilute $\text{HNO}_3$ or $\text{HClO}_4$ pH 4.5 at 80°C or 45% $\text{K}_2\text{CO}_3$ at 40°C Dilute $\text{HNO}_3$ $\text{Ce}^{+4}$ or $\text{Ag}^{+1}$ catalyst or dil. $\text{H}_2\text{SO}_4/60^\circ\text{C}$ $\text{Ag}^{+1}/\text{S}_2\text{O}_8^{-1}$ in dil. $\text{HNO}_3$ Dilute $\text{H}_2\text{SO}_4$ Dilute $\text{H}_2\text{SO}_4$ at 80°C or dil. $\text{HClO}_4/\text{Cl}^{-1}$ Dilute $\text{HNO}_3$ at 95°C 43% $\text{K}_2\text{CO}_3$ at 75°C
422	$\text{PuO}_2^{+1} \rightarrow \text{PuO}_2^{+2}$	$\text{HNO}_3$ $\text{NH}_2\text{OH}\cdot\text{HCl}$ $\text{I}^{-1}$ $\text{SO}_2$ $\text{V}^{+3}$ or $\text{Ti}^{+3}$	Dilute; slow Slow pH 2; slow Dilute $\text{H}^{+1}$ ; slow $\text{HClO}_4$ ; slow
423	$\text{PuO}_2^{+2} \rightarrow \text{PuO}_2^{+1}$	$\text{I}^{-1}$	pH 2

Separation Techniques

	Redox Reaction	Reagent	Conditions
		SO <sub>2</sub>	H <sup>+</sup>
		Fe <sup>+2</sup>	HClO <sub>4</sub> or HCl
		V <sup>+3</sup> or U <sup>+4</sup>	HClO <sub>4</sub>
		HNO <sub>2</sub>	dil. HNO <sub>3</sub> /NaNO <sub>3</sub>
		Ag	dil. HCl
424	PuO <sub>2</sub> <sup>+2</sup> → Pu <sup>+4</sup>	C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	75 °C; RT with dil. HCl
		I <sup>-1</sup>	HNO <sub>3</sub>
		Fe <sup>+2</sup>	HCl, HNO <sub>3</sub> , or H <sub>2</sub> SO <sub>4</sub>
		Sn <sup>+2</sup>	HCl/HClO <sub>4</sub>
		H <sub>2</sub> O <sub>2</sub>	HNO <sub>3</sub> ; continues to Pu <sup>+3</sup> in absence of Fe <sup>+3</sup>
		Ti <sup>+3</sup>	HClO <sub>4</sub>
		Cu <sub>2</sub> O	45% K <sub>2</sub> CO <sub>3</sub> 75 °C
		HNO <sub>2</sub>	HNO <sub>3</sub> /75 °C
		Zn	dil. HCl
425	PuO <sub>2</sub> <sup>+1</sup> → Pu <sup>+4</sup>	HNO <sub>2</sub>	slow
426	Pu <sup>+4</sup> → Pu <sup>+3</sup>	NH <sub>2</sub> OH·HCl	dil. HCl, slow
		hydroquinone	dil. HNO <sub>3</sub>
		H <sub>2</sub> /Pt	HCl
427		I <sup>-1</sup>	dil. HCl
		HSO <sub>3</sub> <sup>-1</sup>	dil. HNO <sub>3</sub>
		NH <sub>2</sub> OH·HCl	
		Zn	dil. HCl
		SO <sub>2</sub>	dil. HNO <sub>3</sub>
		Ti <sup>+3</sup>	HCl, dil. H <sub>2</sub> SO <sub>4</sub> , or dil. HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub>
		ascorbic acid	HNO <sub>3</sub>
		U <sup>+4</sup>	dil. HClO <sub>4</sub>
		H <sub>2</sub> S	dil. acid
428	Tc <sup>+4</sup> → TcO <sub>4</sub> <sup>-1</sup>	HNO <sub>3</sub>	
		H <sub>2</sub> O <sub>2</sub>	
		O <sub>2</sub> (air)	
429	TcO <sub>2</sub> (hydrated) →	Ce <sup>+4</sup>	
430	TcO <sub>4</sub> <sup>-1</sup>		
431	TcCl <sub>6</sub> <sup>-2</sup> → TcO <sub>4</sub> <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub>	
		HNO <sub>3</sub>	
		H <sub>2</sub> O <sub>2</sub>	
		Cl <sub>2</sub>	
		Ce <sup>+4</sup>	
		MnO <sub>4</sub> <sup>-1</sup>	
432	TcO <sub>4</sub> <sup>-1</sup> → Tc <sup>+4</sup> or	N <sub>2</sub> H <sub>4</sub>	dil. H <sub>2</sub> SO <sub>4</sub>
433	TcO <sub>2</sub> (hyd)	NH <sub>2</sub> OH	dil. H <sub>2</sub> SO <sub>4</sub>
		ascorbic acid	dil. H <sub>2</sub> SO <sub>4</sub>

Redox Reaction	Reagent	Conditions
	Sn <sup>+2</sup>	dil. H <sub>2</sub> SO <sub>4</sub>
	Zn	dil. HCl
	Conc. HCl	to TcCl <sub>6</sub> <sup>-2</sup>
434 U <sup>+3</sup> → U <sup>+4</sup>	ClO <sub>4</sub> <sup>-1</sup>	dil. HClO <sub>4</sub>
	Co <sup>+3</sup> complexes	dil. HClO <sub>4</sub> or LiClO <sub>4</sub>
	Cr <sup>+3</sup> and Cr <sup>+3</sup> complexes	dil. HClO <sub>4</sub> or LiClO <sub>4</sub>
	H <sub>2</sub> O	dil. or conc. HCl or H <sub>2</sub> SO <sub>4</sub>
	UO <sub>2</sub> <sup>+1</sup>	dil. HClO <sub>4</sub>
	UO <sub>2</sub> <sup>+2</sup>	dil. HClO <sub>4</sub>
	O <sub>2</sub> (air)	
435 U <sup>+4</sup> → UO <sub>2</sub> <sup>+2</sup>	Br <sub>2</sub>	catalyzed by Fe <sup>+3</sup> or Mn <sup>+2</sup>
	BrO <sub>3</sub> <sup>-1</sup>	HClO <sub>4</sub>
	Ce <sup>+4</sup>	dil. HClO <sub>4</sub>
	ClO <sub>3</sub> <sup>-1</sup>	catalyzed by Fe <sup>+2</sup> or V <sup>+5</sup>
	Fe <sup>+3</sup>	
	HClO <sub>2</sub>	phenol
	HCrO <sub>4</sub> <sup>-1</sup>	
	HNO <sub>2</sub>	catalyzed by Fe <sup>+2</sup>
	HNO <sub>3</sub>	
	H <sub>2</sub> O <sub>2</sub>	
	O <sub>2</sub>	
	Pu <sup>+4</sup>	
	PuO <sub>2</sub> <sup>+2</sup>	
	MnO <sub>2</sub>	
436 UO <sub>2</sub> <sup>+1</sup> → UO <sub>2</sub> <sup>+2</sup>	Fe <sup>+3</sup>	
437 UO <sub>2</sub> <sup>+2</sup> → U <sup>+4</sup>	Cr <sup>+2</sup>	
	Eu <sup>+2</sup>	
	Np <sup>+3</sup>	
	Ti <sup>+3</sup>	
	V <sup>+2</sup> and V <sup>+3</sup>	
438 UO <sub>2</sub> <sup>+2</sup> → U <sup>+3</sup>	Zn(Hg)	
439 UO <sub>2</sub> <sup>+1</sup> → U <sup>+4</sup>	Cr <sup>+2</sup>	
	H <sub>2</sub>	
	Zn(Hg)	

(1) Compiled from: Anders, 1960; Bailar et al., 1984; Bate and Leddicotte, 1961; Cobble, 1964; Coleman, 1965; Cotton and Wilkinson, 1988; Greenwood and Earnshaw, 1984; Hassinsky and Adloff, 1965; Kleinberg and Cowan, 1960; Kolthoff et al., 1969; Latimer, 1952; Metz and Waterbury, 1962; Schulz and Penneman, 1986; Weigel, 1986; and Weigel et al., 1986.

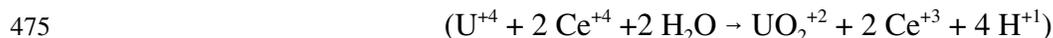
444 In some radioanalytical procedures, establishing different states at different steps in the procedure  
445 is necessary to ensure the requisite chemical behavior of the analyte.

446 One method for the analysis of  $^{129}\text{I}$  in aqueous solutions illustrates the use of oxidation and  
447 reduction chemistry to bring the radionuclide to a specific oxidation state so that it can be  
448 isolated from other radionuclides and other elements (DOE, 1995, Method RP230). Iodine  
449 species in the water sample are first oxidized to iodate ( $\text{IO}_3^{-1}$ ) by sodium hypochlorite ( $\text{NaClO}$ ),  
450 and then reduced to iodide ( $\text{I}^{-1}$ ) by sodium bisulfite. The iodine is finally oxidized to molecular  
451 iodine ( $\text{I}_2$ ) and extracted from most other radionuclides and elements in solution by a nonpolar  
452 organic solvent such as carbon tetrachloride ( $\text{CCl}_4$ ) or chloroform ( $\text{CHCl}_3$ ) (see Section 14.4,  
453 “Solvent Extraction”).

454 Plutonium and its tracers can be equilibrated in a reproducible mixture of oxidation states by the  
455 rapid reduction of all forms of the ion to the +3 state, momentarily, with iodide ion ( $\text{I}^{-1}$ ) in acid  
456 solution. Disproportionation begins immediately, but all radionuclide forms of the analyte and  
457 tracer begin at the same time from the same oxidation state, and a true equilibrium mixture of the  
458 radionuclide and its tracer is achieved. All plutonium radionuclides in the same oxidation state  
459 can be expected to behave the same chemically in subsequent separation and detection  
460 procedures.

461 In addition to dissolution and separation strategies, oxidation-reduction processes are used in  
462 several quantitation steps of radiochemical analyses. These processes include titration of the  
463 analyte and electrochemical deposition on a target for counting.

464 The classical titrimetric method is not commonly employed in the quantitation of environmental  
465 level samples because the concentrations of radionuclides in these samples are typically too low  
466 for detection of the endpoint of the titration, even by electrometric or spectroscopic means.  
467 However, the method is used for the determination of radionuclides in other samples containing  
468 larger quantities of long-lived radionuclides. Millimole quantities of uranium and plutonium in  
469 nuclear fuels have been determined by titration using methods of endpoint detection as well as  
470 chemical indicators (IAEA, 1972). In one method, uranium in the +6 oxidation state is reduced to  
471 +3 and +4 with  $\text{Ti}^{+3}$ , and that in the +3 state is oxidized to +4 with air bubbles (Baetsel and  
472 Demildt, 1972). The solution is then treated with a slight excess of  $\text{Ce}^{+4}$  solution of known  
473 concentration, which oxidizes  $\text{U}^{+4}$  to  $\text{U}^{+6}$  (as  $\text{UO}_2^{+2}$ ) while being reduced, as follows:



476 The excess  $\text{Ce}^{+4}$  is back-titrated with  $\text{Fe}^{+2}$  solution, using ferrion as indicator for the endpoint of  
477 the titration:



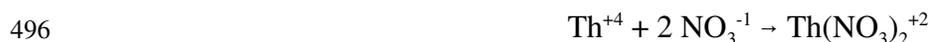
479 Electrochemical methods are typically used in radiochemistry to reduce ions in solution, plating  
480 them onto a target metal for counting. Americium ions ( $\text{Am}^{+3}$ ) from soil samples are ultimately  
481 reduced from solution onto a platinum (Pt) electrode by application of an electrical current in an  
482 electrolytic cell (DOE, 1990 and 1997, Method Am-01). The amount of americium on the  
483 electrode is determined by alpha spectrometry.

484 In some cases, the deposition process occurs spontaneously without the necessity of an applied  
485 current. Polonium (Po) and lead (Pb) spontaneously deposit from a solution of hydrochloric acid  
486 (HCl) onto a nickel (Ni) disk at 85 °C (Blanchard, 1966). Alpha and beta counting are used to  
487 determine  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ . Wahl and Bonner (1951, pp. 460-465) contains a table of  
488 electrochemical methods used for the oxidation and reduction of carrier-free tracers.

## 489 14.3 Complexation

### 490 14.3.1 Introduction

491 A *complex ion* is formed when a metal atom or ion bonds with one or more molecules or anions  
492 through an atom capable of donating one or more electron pairs. A *ligand* is any molecule or ion  
493 that has at least one electron pair that can be donated to the metal. The bond is called a  
494 *coordination bond*, and a compound containing a complex ion is a *coordination compound*. The  
495 following are several examples of the formation of complex ions:



499 \*  $\text{EDTA}^{-4}$  = Ethylenediaminetetraacetate,  $(^{-1}\text{OOC})_2\text{-NH-CH}_2\text{-CH}_2\text{-NH-(COO}^{-1})_2$

500 In a fundamental sense, every ion in solution can be considered complexed; there are no free or  
501 “naked” ions. Dissolved ions are surrounded by solvent molecules. In aqueous solutions, the

502 complexed water molecules, referred to as the *inner hydration sphere*, form aquo ions that can be  
 503 either weakly or strongly bound:



505 From an elementary standpoint, the process of complexation is simply the dynamic process of  
 506 replacing one set of ligands, the solvent molecules, with another. The complexation of a metal  
 507 ion in aqueous solution with a ligand, L, can be expressed as:



509 Successive aquo groups can be replaced by other ligand groups until the complex  $\text{ML}_n^{x-ny}$  is  
 510 formed as follows:



512 In the absence of other complexing agents, in dilute aqueous solution solvated metal ions are  
 513 simply written as  $\text{M}^{+n}$  for simplicity.

514 Ligands are classified by the number of electrons they donate to the metal to form coordination  
 515 bonds to the metal. If only one atom in the ligand is bonded to the metal, it is called a unidentate  
 516 ligand (*dentate* is from the Latin word for teeth. It is a categorization of ligands that describe the  
 517 number of atoms with electron pairs a ligand has available for donation in complex-ion  
 518 formation; if two atoms, bidentate, and so on for tridentate, tetradentate, pentadentate, and  
 519 hexadentate.) The term *coordination number* is also used to indicate the number of atoms  
 520 donating electrons to the metal atom. The coordination number is five in  $\text{U}(\text{CO}_3)_5^{-6}$ , as illustrated  
 521 above. EDTA, also illustrated above, is a hexadentate ligand, because it bonds to the metal  
 522 through the four oxygen atoms and two nitrogen atoms.

523 Table 14.4 lists some common ligands arranged by type.

524 **TABLE 14.4 — Common ligands**

Ligand Type <sup>(1)</sup>	Examples
Unidentate	Water (H <sub>2</sub> O), halides (X <sup>-1</sup> ), hydroxide (OH <sup>-1</sup> ), ammonia (NH <sub>3</sub> ), cyanide (CN <sup>-1</sup> ), nitrite (NO <sub>2</sub> <sup>-1</sup> ), thiocyanate (SCN <sup>-1</sup> ), carbon monoxide (CO)
Bidentate	Oxalate, ethylenediamine, citrate
Tridentate	Diethylenetriamine, 1,3,5 triaminocyclohexane

Ligand Type <sup>(1)</sup>	Examples
Polydentate	8-hydroxyquinoline, $\beta$ -diketones (acetylacetone-2-thenoyltrifluoroacetone [TTA]), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), organophosphates: (octyl(phenyl)- <i>N,N</i> -diiso-butylcarbamoyl-methylphosphine oxide [CMPO]); tributyl phosphate (TBP), trioctylphosphinic oxide (TOPO), quaternary amines (tricaprylyl-methylammonium chloride [Aliquat-336]), triiso-octylamine (TIOA), tri- <i>n</i> -octylamine (TnOA), macrocyclic polyethers (crown ethers such as [18]-crown-6), cryptates

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- (1) Ligands are categorized by the number of electron pairs available for donation. Unidentate ligands donate one pair of electrons; bidentate donate two pairs, etc.

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A ligand can be characterized by the nature and basicity of its ligand atom. Oxygen donors and the fluoride ion are general complexing agents; they combine with any metal ion (cation) with a charge of more than one. Acetates, citrates, tartrate, and  $\beta$ -diketones generally complex all metals. Conversely, cyanide ( $\text{CN}^{-1}$ ), the heavy halides, sulfur donors, and—to a smaller extent—nitrogen donors, are more selective complexing agents than the oxygen donors. These ligands do not complex the A-metals of the periodic table; only the cations of the B-metals and the transition metals coordinate to carbon, sulfur, nitrogen, chlorine, bromine, and iodine.

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### 14.3.2 Chelates

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When a multidentate ligand is bound to the metal atom or ion by two or more electron pairs, forming a ring structure, it is referred to as a *chelate* and the multidentate ligand is called a chelating agent or reagent. Chelates are organic compounds containing two, four, or six carboxylic acid ( $\text{RCOOH}$ ) or amine ( $\text{RNH}_2$ ) functional groups. A chelate is effective at a pH where the acid groups are in the anionic form as carboxylates,  $\text{RCOO}^{-1}$ , but the nitrogen is not protonated so that its lone pair of electrons is free for bonding. The chelate bonds to the metal through the lone pair of electrons of these groups as bi, tetra, or hexadentate ligands, forming a coordination complex with the metal. Binding through multiple sites wraps up the metal in a claw-like fashion, thus the name chelate, which means claw. Practically all chelates form five- or six-membered rings on coordinating with the metal. Chelates are much more stable than complex compounds formed by unidentate reagents. Moreover, if multiple ring systems are formed with a single metal atom or ion, stability improves. For example, ethylenediaminetetraacetic acid (EDTA), a hexadentate ligand, forms especially stable complexes with most metals. As illustrated in Figure 14.1, EDTA has two donor pairs from the nitrogen atoms, and four donor pairs from the oxygen atoms.

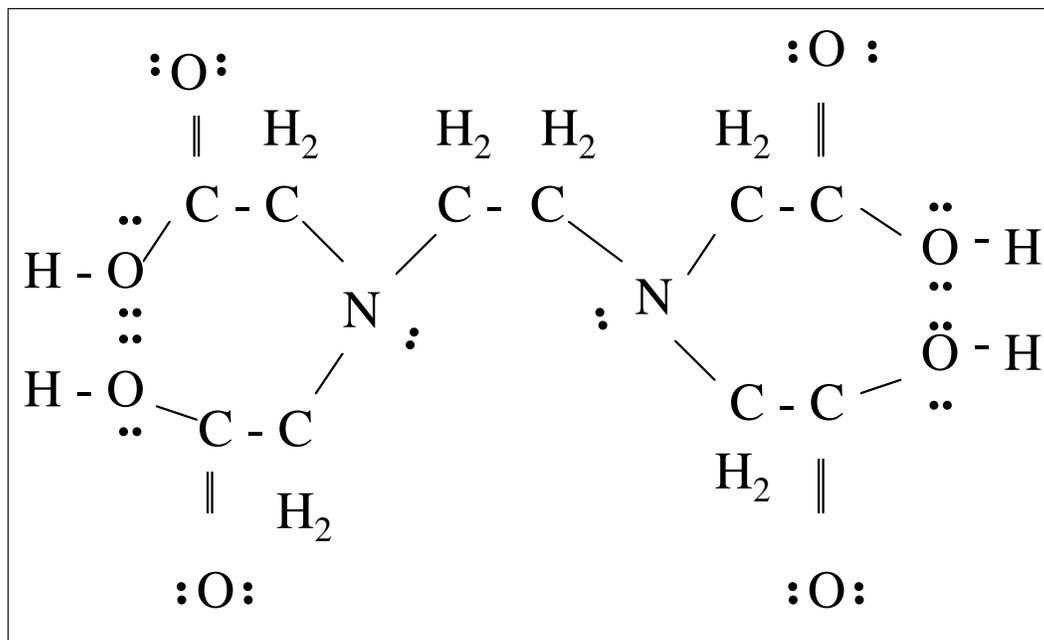


FIGURE 14.1 — Ethylenediaminetetraacetic Acid <sup>(1)</sup> (EDTA)

555 (1) EDTA forms very stable complexes with most metal atoms because it has two pairs of electrons available from  
 556 the nitrogen atoms, and four pairs of electrons from the oxygen atoms. It is often used as a complexing agent in  
 557 a basic solution. Under these conditions, the four carboxylic-acid groups ionize with the loss of a hydrogen ion  
 558 ( $H^+$ ), forming ethylenediaminetetraacetate ( $EDTA^{4-}$ ), a stronger complexing agent. EDTA is often used as a  
 559 food additive to increase shelf life, because it combines with transition metal ions that catalyze the decompo-  
 560 sition of food. It is also used as a water softener to remove calcium ( $Ca^{+2}$ ) and magnesium ( $Mg^{+2}$ ) ions from  
 561 hard water.

562 Various chelating agents bind more readily to certain cations, providing the specificity for  
 563 separating ions by selective bonding. Usually, the complex is insoluble under the solvent  
 564 conditions used, allowing the collection of the complex by precipitation. Selectivity of a chelate  
 565 can be partially controlled by adjusting the pH of the medium to vary the net charge on its  
 566 functional groups. Different chelates provide specificity through the number of functional groups  
 567 available for bonding and the size of claw formed by the molecular structure, providing a select  
 568 fit for the diameter of a specific cation. The electron-donating atoms of the chelate form a ring  
 569 system with the metal atom when they participate in the coordination bond. In most cases,  
 570 chelates form much more stable complexes than unidentate ligands. For example, the complex  
 571 ion formed between  $Ni^{+2}$  and the bidentate ligand ethylenediamine ( $H_2N-CH_2-CH_2-NH_2$ , or en),  
 572  $Ni(en)_3^{+2}$ , is almost  $10^8$  times more stable than the complex ion formed between the metal ion  
 573 and ammonia,  $Ni(NH_3)^{+2}$ .

574 Another class of ligands that is becoming increasingly important to the radiochemist doing  
 575 laboratory analyses is the macrocyclic polyethers, commonly called *crown ethers* (Horwitz et al.,  
 576 1991 and 1992; Smith et al., 1996 and 1997). These compounds are cyclic ethers containing a  
 577 number of regularly spaced oxygen atoms. Some examples are given in Figure 14.2.

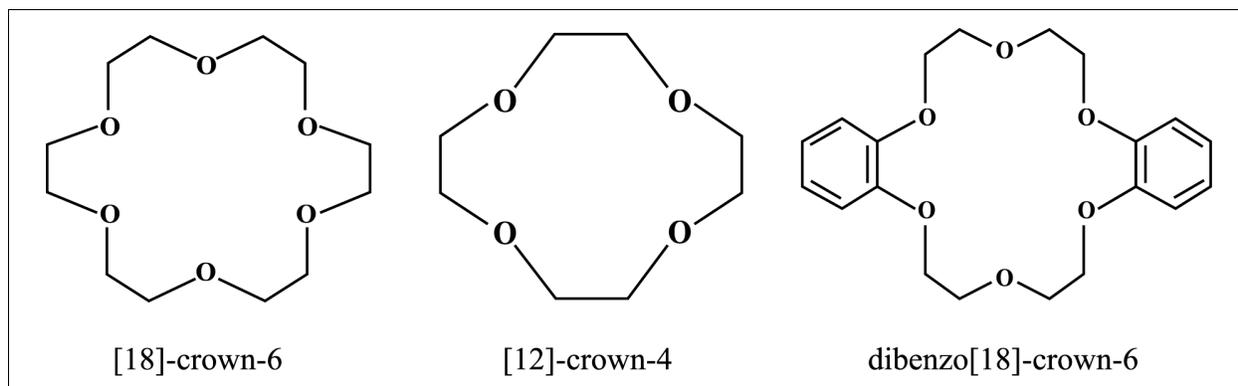


FIGURE 14.2 — Crown ethers

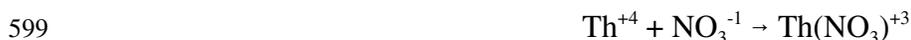
578 First identified in 1967, crown ethers have been shown to form particularly stable coordination  
 579 complexes. The term, “crown ether,” was suggested by the three-dimensional shape of the  
 580 molecule. In the common names of the crown ethers, the ring size is given in brackets, and the  
 581 number of oxygen atoms follows the word “crown.”

582 Crown ethers have been shown to react rapidly and with high selectivity (Gokel, 1991; Hiraoka,  
 583 1992). This property is particularly significant when a separation requires high selectivity and  
 584 efficiency in removing low-level species from complex and concentrated matrices, a situation  
 585 frequently encountered in environmental or mixed-waste analyses. Because crown ethers are  
 586 multidentate chelating ligands, they have very high formation constants. Moreover, because the  
 587 metal ion must fit within the cavity, crown ethers demonstrate some selectivity for metal ions  
 588 according to their size. Crown ethers can be designed to be very selective by changing the ring  
 589 size, the ring substituents, the ring number, the donor atom type, etc. For example, dibenzo-18-  
 590 crown-6 forms a strong complex with potassium; weaker complexes with sodium, cesium, and  
 591 rubidium; and no complex with lithium or ammonium, while 12-crown-4, with its smaller cavity,  
 592 specifically complexes with lithium.

593 Other crown ethers are selective for radionuclide ions such as radium and  $\text{UO}_2^{+2}$ . Addition of 18-  
 594 crown-6 to solutions containing  $\text{NpO}_2^{+2}$  causes the reduction of neptunium to  $\text{Np(V)}$  as  $\text{NpO}_2^{+1}$ ,  
 595 which is encircled by the ether ligand (Clark et al., 1998).

596 **14.3.3 The Formation (Stability) Constant**

597 The stability of the complex is represented by the magnitude of an equilibrium constant  
598 representing its formation. The complex ion,  $[\text{Th}(\text{NO}_3)_2^{+2}]$ , forms in two equilibrium steps:



601 The *stepwise formation (stability) constants* are:

602 
$$K_1 = \frac{[\text{Th}(\text{NO}_3)^{+3}]}{[\text{Th}^{+4}][\text{NO}_3^{-1}]}$$

603 and

604 
$$K_2 = \frac{[\text{Th}(\text{NO}_3)_2^{+2}]}{[\text{Th}(\text{NO}_3)^{+3}][\text{NO}_3^{-1}]}$$

605 The *overall formation (stability) constant* is:

606 
$$K = \frac{[\text{Th}(\text{NO}_3)_2^{+2}]}{[\text{Th}^{+4}][\text{NO}_3^{-1}]^2}$$

607 which can be calculated from  $K_1$  and  $K_2$ :

608 
$$K = K_1 \times K_2.$$

609 In the  $\text{Ni}^{+2}$  examples cited in the preceding section, the relative stabilities of the complex ions are  
610 represented by the values of  $K$ ; for  $\text{Ni}(\text{en})_3^{+2}$  it is  $10^{18.28}$ , and for  $\text{Ni}(\text{NH}_3)_6^{+2}$  it is  $10^{8.61}$  (Cotton and  
611 Wilkinson, 1988, p. 45).

612 Many radionuclides form stable complex ions and coordination compounds that are important to  
613 the separation and determination steps in radioanalytical chemistry. Formation of a complex  
614 changes the properties of the ion in several ways. For example:

- 615 • Complexation of  $\text{UO}_2^{+2}$  with carbonate to form  $\text{UO}_2(\text{CO}_3)_4^{-4}$  increases the solubility of the  
616 uranium species in groundwater (Lindsay, 1988, p. 9.2-19).

- 617 • Th<sup>+2</sup> forms Th(NO<sub>3</sub>)<sub>6</sub><sup>-2</sup> in nitric acid solution (optimally at 7 M) that is the basis for separation  
 618 of thorium from other actinides and thorium progeny, because they do not form anionic  
 619 complexes under these conditions (Hyde, 1960, p. 25).
- 620 • Ra<sup>+2</sup> form a very insoluble compound with sulfate (RaSO<sub>4</sub>) but is soluble in hot concentrated  
 621 sulfuric acid because of the formation of Ra(SO<sub>4</sub>)<sub>2</sub><sup>-2</sup> (Kirby and Salutsky, 1964, p. 9).

622 In addition, the complex ion in solution is in equilibrium with the free (hydrated) ion, and the  
 623 equilibrium mixture might, therefore, contain sufficient concentration of the free ion for it to be  
 624 available for other reactions, depending on the stability of the complex ion:



626 **14.3.4 Complexation and Radiochemical Analysis**

627 Property changes also accompany the formation of complex ions and coordination compounds  
 628 from simple radionuclide ions. These changes provide a valuable approach in radiochemistry for  
 629 isolating, separating, and measuring radionuclide concentrations, and are important in several  
 630 areas of radiochemistry.

631 14.3.4.1 Extraction of Laboratory Samples and Ores

632 Uranium ores are leached with alkaline carbonates to dissolve uranium as the UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>-4</sup>  
 633 complex ion after oxygen is used to convert U<sup>+4</sup> to U<sup>+6</sup> (Grindler, 1962, p. 256). Samples  
 634 containing refractory plutonium oxides are dissolved with the aid of a nitric acid-hydrofluoric  
 635 acid solution to produce the complex cation PuF<sup>+3</sup> and similar cationic fluorocomplexes  
 636 (Booman and Rein, 1962, p. 244). Refractory silicates containing niobium (Nb) also yield to  
 637 fluoride treatment. Potassium bifluoride (KF<sub>2</sub><sup>-1</sup>) is used as a low-temperature flux to produce a  
 638 fluoride complex NbF<sub>6</sub><sup>-1</sup> (Willard and Rulfs, 1961, p. 1046; Greenwood and Earnshaw, 1984,  
 639 p. 1158).

640 14.3.4.2 Separation by Solvent Extraction and Ion-Exchange Chromatography

641 Many ion-exchange separations of radionuclides are based on the formation of complex ions  
 642 from the metal ions in solution or the displacement of ions bound to an exchanger by complex  
 643 formation. Uranium in urine samples, for example, is partly purified by forming a chlorocomplex  
 644 of U<sup>+4</sup> and UO<sub>2</sub><sup>+2</sup> ions, UCl<sub>6</sub><sup>-2</sup> and UO<sub>2</sub>Cl<sub>3</sub><sup>-1</sup>, that bind preferentially to the anion-exchange ligands

645 in 7 M HCl. Other cations pass through the column under these conditions. Uranium is  
646 subsequently eluted with 1 M HCl (DOE, 1990 and 1997, Method U-01).

647 For separation on a larger scale—such as in an industrial setting—chelates are often used in a  
648 column chromatography or filtration unit. They are immobilized by bonding to an inert matrix,  
649 such as polystyrene or an alumina/silica material. A solution containing the ions to be separated  
650 is passed continuously through the column or over the filter, where the select cations are bonded  
651 to the chelate as the other ions pass through. Washing the column or filter with a solution at  
652 alternate pH or ionic strength will permit the elution of the bound cation.

653 Tetrapositive thorium (Th) is adsorbed more strongly by cation exchangers than most other  
654 cations (Hyde, 1960, pp. 21-23). The adsorbed thorium is separated from most other ions by  
655 washing the column with mineral acids or other eluting agents. Even the tetrapositive plutonium  
656 ion,  $\text{Pu}^{+4}$ , and the uranyl ion,  $\text{UO}_2^{+2}$ , are washed off with high concentrations of HCl because they  
657 form chlorocomplexes,  $\text{PuCl}_6^{-2}$  and  $\text{UO}_2\text{Cl}_3^{-1}$ , respectively. Thorium is then removed by eluting  
658 with a suitable complexing agent such as oxalate, which reduces the effective concentration of  
659  $\text{Th}^{+4}$ , reversing the adsorption process. Using oxalate,  $\text{Th}(\text{C}_2\text{O}_4)_4^{-4}$  forms and the anion is not  
660 attracted to the cation exchanger.

#### 661 14.3.4.3 Formation and Dissolution of Precipitates

662 A classical procedure for the separation and determination of nickel (Ni) is the precipitation of  
663  $\text{Ni}^{+2}$  with dimethylglyoxime, a bidentate ligand that forms a highly selective, stable chelate  
664 complex with the ion,  $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2^{-1})_2$  (DOE, 1995, Method RP300). Uranium in the +4  
665 oxidation state can also be precipitated from acidic solutions with a chelating agent, cupferron  
666 (ammonium nitrosophenylhydroxylamine,  $\text{C}_8\text{H}_5(\text{NO})\text{O}^{-1}\text{NH}_4^{+1}$ ) (Grindler, 1962, p. 256). In  
667 another procedure,  $\text{Co}^{+2}$  can be selectively precipitated from solution as  $\text{K}_3\text{Co}(\text{NO}_2)_6$ . In this  
668 procedure, cobalt, which forms the largest number of complexes of all the metals, forms a  
669 complex anion with six nitrite ligands,  $\text{Co}(\text{NO}_2)_6^{-3}$  (EPA, 1973, pp. 53-58).

670 In radiochemical separations and purification procedures, precipitates of radionuclides are  
671 commonly redissolved to release the metal ion for further purification or determination. In the  
672 determination of  $^{90}\text{Sr}$ , strontium ( $\text{Sr}^{+2}$ ) is separated from the bulk of the solution by direct  
673 precipitation of the sulfate,  $\text{SrSO}_4$ . The precipitate is redissolved by forming a complex ion with  
674 EDTA,  $\text{Sr}(\text{EDTA})^{-2}$ , to separate it from lanthanides and actinides (DOE, 1995, Method RP520).  
675 Radium also forms a very stable complex with EDTA. Solubilization of radium,  $\text{Ra}^{+2}$ ,  
676 coprecipitated with barium sulfate ( $\text{BaSO}_4$ ) is used in the  $^{228}\text{Ra}$  determination of drinking water  
677 by using EDTA (EPA, 1980, pp. 49-57).

678 14.3.4.4 Stabilization of Ions in Solution

679 In some radiochemical procedures, select radionuclides are separated from other elements and  
680 other radionuclides by stabilizing the ions as complex ions, while the other substances are  
681 precipitated from solution. In a procedure extensively used at Oak Ridge National Laboratory  
682 (ORNL),  $^{95}\text{Nb}$  is determined in solutions by taking advantage of complex-ion formation to  
683 stabilize the ion ( $\text{Nb}^{+5}$ ) in solution during several steps of the procedure (Kallmann, 1964,  
684 pp. 343-344). The niobium sample and carrier are complexed with oxalic acid in acidic solution  
685 to prevent precipitation of the carrier and to promote interchange between the carrier and  $^{95}\text{Nb}$ .  
686 Niobium is precipitated as the pentoxide after warming the solution to destroy the oxalate ion,  
687 separating it from the bulk of other ions in solution. Niobium is also separated specifically from  
688 zirconium by dissolving the zirconium oxide in hydrofluoric acid.

689 14.3.4.5 Detection and Determination

690 Compleximetric titration of metal ions with EDTA using colorimetric indicators to detect the  
691 endpoint can be used for determination procedures. Uranium does not form a selective complex  
692 with EDTA, but this chelate has been used to titrate pure uranium solutions (Grindler, 1962,  
693 p. 94). The soluble EDTA complex of thorium is the basis of a titrimetric determination of small  
694 amounts of thorium (Hyde, 1960, p. 9).

695 Spectrometric determinations are also based on the formation of complex ions. Microgram  
696 quantities of uranium are determined by the absorbance at 415 nm (a colorimetric determination)  
697 of the uranyl chelate complex with dibenzoylmethane,  $\text{C}_6\text{H}_5\text{-CO-CH}_2\text{-CO-C}_6\text{H}_5$  (Grindler, 1962,  
698 pp. 271-276).

699 **14.4 Solvent Extraction**

700 **14.4.1 Extraction Principles**

701 Since the early days of the Manhattan Project, when scientists extracted uranyl nitrate into diethyl  
702 ether to purify the uranium used in the first reactors, solvent extraction has been an important  
703 separation technique for radiochemists. Solvent extraction, or liquid-liquid extraction, is a  
704 technique used both in the laboratory and on the industrial scale. However, current laboratory  
705 trends are away from this technique, mainly because of the costs of materials and because it is  
706 becoming more difficult and costly to dispose of the mixed waste generated from the large  
707 volumes of solvents required. The technique also tends to be labor intensive because of the need

708 for multiple extractions using separatory funnels. Nonetheless, solvent extraction remains a  
709 powerful separation technique worthy of consideration.

710 *Solvent extraction* refers to the process of selectively removing a solute from a liquid mixture  
711 with a solvent. As a separation technique, it is a partitioning process based on the unequal  
712 distribution of the solute (A) between two immiscible solvents, usually water (aq) and an organic  
713 liquid (org):



715 The solute can be in a solid or liquid form. The extracting solvent can be water, a water-miscible  
716 solvent, or a water-immiscible solvent; but it must be insoluble in the solvent of the liquid  
717 mixture. Solutes exhibit different solubilities in various solvents. Therefore, the choice of  
718 extracting solvent will depend upon the properties of solute, the liquid mixture, as well as other  
719 requirements of the experimental procedure. The solvents in many applications are water and a  
720 nonpolar organic liquid, such as hexane or diethyl ether, but other solvent pairs are commonly  
721 used. In general terms, the solute to be removed along with impurities or interfering analytes to  
722 be separated are already dissolved in one of the solvents (water, for example). In this example, a  
723 nonpolar organic solvent is added and the two are thoroughly mixed, usually by shaking in a  
724 separatory funnel. Shaking produces a fine dispersion of each solvent in the other that will  
725 separate into two distinct layers after standing for several minutes. The more dense solvent will  
726 form as the bottom layer. Separation is achieved because the solute and accompanying impurities  
727 or analytes have different solubilities in the two solvents. The solute, for example, might  
728 preferentially remain in the aqueous phase, while the impurities or analyte selectively dissolve in  
729 the organic phase. The impurities and analyte are *extracted* from the aqueous layer into the  
730 organic layer. Alternatively, the solute might be more soluble in the organic solvent and will be  
731 extracted from the aqueous layer into the organic layer, leaving the impurities behind in the  
732 aqueous layer.

#### 733 **14.4.2 Distribution Coefficient**

734 The different solubilities of a solute in the solvent pairs of an extraction system are described by  
735 the *distribution* or *partition coefficient*,  $K_d$ . The coefficient is an equilibrium constant that  
736 represents the solubility of the solute in one solvent relative to its solubility in another solvent.  
737 Once equilibrium is established, the concentration of solute in one phase has a direct relationship  
738 to the solute concentration in the other phase. This is expressed mathematically by:

739 
$$K_d = [A_{\text{org}}] / [A_{\text{aq}}]$$

740 where  $[A_{\text{org}}]$  and  $[A_{\text{aq}}]$  are the concentration of the solute in the organic and aqueous phase  
 741 respectively, and  $K_d$  is a constant. The concentrations are typically expressed in units of moles/kg  
 742 (molality) or g/g; therefore, the constant is unitless. These solubilities usually represent saturated  
 743 concentrations for the solute in each solvent. Because the solubilities vary with temperature, the  
 744 coefficient is temperature-dependent, but not by a constant factor. Wahl and Bonner (1951, pp.  
 745 434-439) contains a table of solvent extraction systems for carrier-free tracers containing  
 746 laboratory conditions and distribution coefficients.

747 A distribution coefficient of 90 for a solute in a hexane/water system, for example, means that  
 748 the solute is 90 times more soluble at saturation conditions in hexane than in water, but note that  
 749 some of the water still contains a small amount of the solute. Solvent extraction selectively  
 750 dissolves the solute in one solvent, but it does not remove the solute completely from the other  
 751 solvent. A larger coefficient would indicate that, after extraction, more solute would be  
 752 distributed in hexane relative to water, but a small quantity would still be in the water. Solvent  
 753 extraction procedures often use repeated extractions to extract a solute quantitatively from a  
 754 liquid mixture.

755 The expression of the distribution law is only a very useful approximation; it is not thermo-  
 756 dynamically rigorous, nor does it account for situations in which the solute is involved in a  
 757 chemical reaction, such as dissociation or association, in either phase. Consider, for example,  
 758 dimerization in the organic phase:



760 where the distribution ratio,  $D$ , is an alternate form of the distribution coefficient expressed by:

761 
$$D = ([A_{\text{org}}]_{\text{monomer}} + [A_{\text{org}}]_{\text{dimer}}) / [A_{\text{aq}}]$$

762 or

763 
$$D = ([A_{\text{org}}] + 2 [(A)_{2, \text{org}}]) / [A_{\text{aq}}]$$

764 Because the concentration of the monomer that represents the dimeric form of the solute is twice  
 765 that of the concentration of the dimer:

766 
$$[A_{\text{org}}]_{\text{dimer}} = 2[(A)_{2, \text{org}}]$$

767 Substitution of  $K_d$  produces:

768 
$$D = K_d(1 + 2K_2 [A_{\text{org}}])$$

769 where  $K_2$  is the dimerization constant,  $K_2 = [(A)_{2,org}]/[A_{org}]^2$ . Because dimerization decreases the  
770 concentration of the monomer, the species that takes part directly in the phase partition, the  
771 overall distribution increases.

### 772 14.4.3 Extraction Technique

773 There is extensive literature on the topic of extraction technique, but only a few sources are listed  
774 here. The theory of solvent extraction is covered thoroughly in Irving and Williams (1961), Lo et  
775 al. (1983), and Dean (1995). Moreover, the journal *Solvent Extraction and Ion Exchange* is an  
776 excellent source for current advances in this field. A practical discussion on the basics of solvent  
777 extraction is found in Korkisch (1969). The discussion applies to a metallic element in solution  
778 as a cation extracted by a nonpolar solvent:

779 “In solvent extraction, the element which is to be separated, contained in an aqueous solution,  
780 is converted to a compound which is soluble in an organic solvent. The organic solvent must  
781 be virtually immiscible with water. By shaking the aqueous solution with the organic solvent  
782 (extractant) in a separating funnel, the element is extracted into the organic phase. After  
783 allowing the aqueous and organic phases to separate in the funnel, the organic extract is  
784 removed from contact with the aqueous layer. This single-stage batch extraction method is  
785 employed when  $K_d$  is relatively large and for a simple separation it is essential that the  
786 distribution coefficients of the metal ions to be separated be sufficiently different. As in the  
787 case of ion exchange, the effectiveness of separation is usually expressed by means of the  
788 separation factor which is given by the ratio of the distribution coefficients of two different  
789 elements which were determined under identical experimental conditions. This ratio  
790 determines the separability of two elements by liquid-liquid extraction. Separations can only  
791 be achieved if this ratio shows a value which is different from unity and they are clean and  
792 can be quickly and easily achieved where one of the distribution coefficients is relatively  
793 large and the other very small (high separation factor).

794 “In those extractions where the separation factor approaches unity, it is necessary to employ  
795 continuous extraction or fractionation methods. With the latter techniques distribution,  
796 transfer and recombination of various fractions are performed a sufficient number of times to  
797 achieve separation. In continuous extraction use is made of a continuous flow of immiscible  
798 solvent through the solution or a continuous counter-current flow of both phases. In  
799 continuous extraction the spent solvent is stripped and recycled by distillation, or fresh  
800 solvent is added continuously from a reservoir. Continuous counter-current extraction  
801 involves a process where the two liquid phases are caused to flow counter to each other.  
802 Large-scale separations are usually performed using this technique.

803 “When employing liquid-liquid extraction techniques, one of the most important  
804 considerations is the selection of a suitable organic solvent. Apart from the fact already  
805 mentioned that it must be virtually immiscible with water, the solubility of the extracted  
806 compound in the solvent must be high if a good separation is to be obtained. Furthermore, it  
807 has to be selective, i.e., has to show the ability to extract one component of a solution in  
808 preference to another. Although the selectivity of a solvent for a given component can be  
809 determined from phase diagrams, it is a little-used procedure in analytical chemistry. The  
810 principal difficulty is simply that too few phase diagrams exist in the literature. The result is  
811 that the choice of an extractant is based on either experience or semi-empirical  
812 considerations. As a rule, however, polar solvents are used for the extraction of polar  
813 substances from nonpolar media, and vice versa. Certainly the interactions of solute and  
814 solvent will have an effect on the selectivity of the solvent. If the solute is readily solvated by  
815 a given solvent, then it will be soluble in that solvent. Hydrogen bond formation between  
816 solute and solvent influences solubility and selectivity.

817 “Almost as important as the selectivity of the extractant is the recovery of the solute from the  
818 organic extract. Recovery can be achieved by distillation or evaporation of the solvent,  
819 provided that the solute is nonvolatile and thermally stable. This technique is, however, less  
820 frequently used than the principle of back extraction (stripping) which involves the treatment  
821 of the organic extract with an aqueous solution containing a reagent which causes the  
822 extracted solute to pass quantitatively into the aqueous layer...

823 “In solvent extraction the specific gravity of the extractant in relation to the aqueous phase is  
824 important. The greater the difference in the solvent densities, the faster will be the rate at  
825 which the immiscible layers separate. Emulsions are more easily produced when the densities  
826 of the two solvents are similar. Sometimes troublesome emulsions can be broken by  
827 introducing a strong electrolyte into the system or by the addition of small quantities of an  
828 aliphatic alcohol” (Korkisch, 1969, pp. 20-22).

829 Korkisch continues:

830 “Liquid-liquid extraction can be applied to the analysis of inorganic materials in two different  
831 ways.

832 (a) Where the element or elements to be determined are extracted into the organic phase.

833 (b) Where the interfering elements are removed by extraction, leaving the element or  
834 elements to be determined in the aqueous phase.

835 “Solvent extraction separations are mainly dependent for their successful operation upon the  
836 distribution ratio of the species between the organic and aqueous phase and the pH and salt  
837 concentration of the aqueous phase. Much of the selectivity which is achieved in liquid-liquid  
838 extraction is dependent upon adequate control of the pH of the solution. The addition of  
839 masking agents such as EDTA and cyanide can greatly improve selectivity, but they too are  
840 dependent upon the pH of the solution to exert their full effect. In many cases complete  
841 extractions and separations are obtained only in the presence of salting-out agent. An  
842 example is the extraction of uranyl nitrate. In the presence of additional nitrate, the increase  
843 in the concentration of the nitrate ion in the aqueous solution shifts the equilibrium between  
844 the uranyl ion and the nitrate complexes toward the formation of the latter, and this facilitates  
845 a more complete extraction of the uranium into the organic solvent. At the same time, the  
846 salting-out agent has another, more general, effect: as its affinity for water is large, it  
847 becomes hydrated by the water molecules so that the substance to be extracted is really  
848 dissolved in a smaller amount of water, and this is the same as if the concentration in the  
849 solution were increased. As a result, the distribution coefficient between the aqueous and the  
850 organic phases is increased. As a rule the salting-out agent also lowers the solubility of the  
851 extractant in the aqueous phase, and this is often important in separations by extraction. The  
852 efficiency of the salting-out action depends upon the nature and the concentration of the  
853 salting-out agent. For the same molar concentration of the salting-out agent its action  
854 increases with an increase in the charge and decrease in the radius of its cation” (Korkisch,  
855 1969, pp. 23-24).

856 A hydrated metal ion will always prefer the aqueous phase to the organic phase because of  
857 hydrogen bonding and dipole interaction in the aqueous phase. Therefore, to get the metal ion to  
858 extract, some or all of the inner hydration sphere must be removed. The resulting complex must  
859 be neutrally charged and organophilic. Removal of the hydration sphere is accomplished by  
860 coordination with an anion to form a neutral complex. Neutral complexes will generally be more  
861 soluble in an organic phase. Larger complexing anions favor the solubility in the organic phase.

862 Extracting agents are thus divided into three classes: polydentate organic anions, neutral organic  
863 molecules, and large organic cations. Many of the multidentate ligands discussed previously are  
864 used in solvent extraction systems.

865 The radioanalytical procedure for uranium (U) and thorium (Th) employs solvent extraction to  
866 separate the analytes before alpha counting (EPA, 1984, pp. U/Th-01-1-14). An aqueous solution  
867 of the two is extracted with a 10 percent solution of triisooctylamine (TIOA) in *para*-xylene to  
868 remove uranium, leaving thorium in the water (Grinder, 1962, pp. 175-180). Each solution is  
869 further processed to recover the respective radionuclides for separate counting.

870 **14.4.4 Solvent Extraction and Radiochemical Analysis**

871 In many purification procedures, separated solutions are used directly in further isolation steps. If  
872 necessary, the substances can be collected by distillation or evaporation of the respective  
873 solvents. In the uranium/thorium procedure described above, the aqueous layer containing  
874 thorium is evaporated, and the thorium is redissolved in an alternate solution before it is purified  
875 further. In other cases, the solution is extracted again to take up the solute in another solvent  
876 before the next step in the procedure. Uranium in TIOA/*p*-xylene, for example, is extracted back  
877 into a nitric acid solution for additional purification (EPA, 1984, pp. U/Th-01-1-U/Th-01-14).

878 In some solvent-extraction procedures, more than one extraction step is required for the  
879 quantitative removal of a solute from its original solvent. The solute is more soluble in one  
880 component of the solvent pair, but not completely insoluble in the other component, so  
881 successive extractions of the aqueous solution of the solute by the organic solvent will remove  
882 more and more of the solute from the water until virtually none remains in the aqueous layer.  
883 Extraction of uranium with TIOA/*p*-xylene, for example, requires two extractions before  
884 quantitative removal is achieved (EPA, 1984, pp. U/Th-01-1-U/Th-01-14). The organic layers  
885 containing the uranium are then combined into one solution for additional processing.

886 Solvent extraction is greatly influenced by the chemical form (ionic or molecular) of the solute to  
887 be extracted, because different forms of the solute can have different solubilities in the solvents.  
888 In the uranium/thorium procedure described above, uranium is extracted from water by  
889 TIOA/hydrochloric acid, but it is stripped from the amine solution when extracted with nitric  
890 acid. Simply changing the anion of uranium and TIOA from chloride to nitrate significantly alters  
891 the complex stability of uranium and TIOA.

892 Organic amines are sometimes converted to their cationic forms, which are much more soluble in  
893 water and much less soluble in organic solvents. The amine is converted to the corresponding  
894 ammonium salt by an acid, such as hydrochloric acid:



896 Correspondingly, carboxylic acids are converted to their carboxylates that are more soluble in  
897 water and less soluble in organic solvents. They are produced by treating the carboxylic acid with  
898 a base, such as sodium hydroxide:



900 Multidentate organic anions that form chelates are important extracting agents. These reagents,  
901 such as the  $\beta$ -diketonates and thenoyltrifluoroacetone (TTA) (Ahrland, 1986, pp. 1518-1521), are  
902 commonly used for extracting the actinide elements. When the aqueous solution and organic  
903 phase come into contact with one another, the chelating agent dissolves in the aqueous phase,  
904 ionizes, and complexes the metal ion; the resulting metal chelate subsequently dissolves in the  
905 organic phase.

906 A number of organophosphorus compounds are also efficient extractants because they and their  
907 complexes are readily soluble in organic solvents. The actinide  $\text{MO}_2^{+2}$  and actinide +4 ions are  
908 very effectively extracted by reagents such as monobasic diethylhexylphosphoric acid (HDEHP)  
909 and dibutylphosphoric acid (HDBP) (Cadieux and Reboul, 1996).

910 Among the neutral compounds, alcohols, ethers, and ketones have been commonly employed as  
911 extractants. Methyl isobutyl ketone was used in one of the early large-scale processes (the Redox  
912 process) to recover uranium and plutonium from irradiated fuel (Choppin et al., 1995, p. 607).  
913 However, the most widely used neutral extractants are the organophosphorus compounds such as  
914 TBP (tributyl phosphate). The actinide elements thorium, uranium, neptunium, and plutonium  
915 easily form complexes with TBP (Choppin et al., 1995, p. 607). Salting-out agents such as  $\text{HNO}_3$   
916 and  $\text{Al}(\text{NO}_3)_3$  are commonly employed to increase extraction in these systems. This chemistry is  
917 the basis of the Purex process used to reprocess spent nuclear fuel (Choppin et al., 1995, pp. 608-  
918 610).

919 An important addition to the Purex process is the solvent extraction procedure known as TRUEX  
920 (*Trans Uranium Extraction*). This process uses the bifunctional extractant CMPO  
921 ([octyl(phenyl)]-N,N-diisobutylcarbonylmethylphosphine oxide) to remove transuranium  
922 elements from the waste solutions generated in the Purex process. This type of compound  
923 extracts actinides at high acidities, and can be stripped at low acidity or with complexing agents.  
924 Many of the recent laboratory procedures for biological waste and environmental samples are  
925 based upon this approach (see Section 14.4.5.1, "Extraction Chromatography Columns").

926 The amines, especially the tertiary and quaternary amines, are strong cationic extractants. These  
927 strong bases form complexes with actinide metal cations. The extraction efficiency improves  
928 when the alkyl groups have long carbon chains, such as in trioctylamine (TnOA) or  
929 triisooctylamine (TIOA). The pertechnetate ion ( $\text{TcO}_4^{-1}$ ) is also extracted by these cationic  
930 extractants (Chen, 1990).

931 Table 14.5 lists common solvent extraction procedures for some radionuclides of interest and  
932 includes the examples described above.

933 **TABLE 14.5 — Radioanalytical methods employing solvent extraction** <sup>(1)</sup>

Analyte	Extraction Conditions (Reference)
<sup>89/90</sup> Sr	From soils and sediments with dicyclohexano-18-crown-6 in trichloromethane with back extraction with EDTA (Pimpl, 1995)
<sup>99</sup> TcO <sub>4</sub> <sup>-</sup>	From dilute H <sub>2</sub> SO <sub>4</sub> solutions into a 5% TnOA in xylene mixture and back extracted with NaOH (Golchert and Sedlet, 1969; Chen, 1990); from dilute H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> , and HCl solutions into a 5% TnOA in xylene (Dale et al., 1996); from HNO <sub>3</sub> into 30% TnOA in xylene and back extracted with NaOH (Hirano, 1989); from dilute H <sub>2</sub> SO <sub>4</sub> solutions into TBP (Holm et al., 1984; Garcia-Leon, 1990); the tetraphenyl arsonium complex of Tc into chloroform (Martin and Hylko, 1987); from K <sub>2</sub> CO <sub>3</sub> with MEK (Paducah R-46); from alkaline nuclear-waste media with crown ethers (Bonnesen et al., 1995)
<sup>210</sup> Pb	As lead bromide from bone, food, urine, feces, blood, air, and water with Aliquat-336 (DOE, 1990 and 1997, Method Pb-01; Morse and Welford, 1971)
Radium through Californium	From soil following KF-pyrosulfate fusion and concentration by barium sulfate precipitation with Aliquat-336 in xylene (Sill et al., 1974)
Actinides	<p data-bbox="397 858 1412 982">From water following concentration by ferric hydroxide precipitation and group separation by bismuth phosphate precipitation, uranium extracted by TOPO, plutonium and neptunium extracted by TIOA from strong HCl, and thorium separated from americium and curium by extraction with TOPO (EPA, 1980, Method 907.0)</p> <p data-bbox="397 993 1412 1056">And other metals from TOPO (NAS-NS 3102) and from high-molecular weight amines such as TIOA (NAS-NS 3101).</p> <p data-bbox="397 1066 1055 1098">Uranium and plutonium from HCl with TIOA (Moore, 1958)</p> <p data-bbox="397 1108 1412 1140">From nitric acid wastes using the TRUEX process with CMPO (Horwitz et al., 1985 and 1987)</p> <p data-bbox="397 1150 1412 1249">With various extractive scintillators followed by PERALS<sup>®</sup> spectrometry (McDowell 1986 and 1992); with HDEHP after extraction chromatography followed by PERALS<sup>®</sup> spectrometry (Cadieux and Reboul, 1996)</p>
Thorium	From aqueous samples after ion exchange with TTA, TIOA, or Aliquat-336 (DOE, 1995, Method RP570)
Uranium	<p data-bbox="397 1335 1412 1398">From waters with ethyl acetate and magnesium nitrate as salting-out agent (EPA, 1980, Method 908.1); with URAEX<sup>™</sup> followed by PERALS<sup>®</sup> spectrometry (Leyba et al., 1995)</p> <p data-bbox="397 1409 1412 1465">From soil, vegetation, fecal ash, and bone ash with Alamine-336 (DOE, 1990 and 1997, Methods Se-01, U-03)</p>

943 (1) This list is representative of the methods found in the literature. It is not an exhaustive compilation, nor does it  
944 imply preference over methods not listed.

#### 945 14.4.5 Solid-Phase Extraction

946 A technique closely related to solvent extraction is solid-phase extraction (SPE). SPE is a  
947 solvent-extraction system in which one of the liquid phases is made stationary by adsorption onto  
948 a solid support, usually silica, and the other liquid phase is mobile. Small columns or membranes

949 are used in the SPE approach. Many of the same extracting agents used in solvent extraction can  
 950 be used in these systems. SPE is becoming widely accepted as an excellent substitute for liquid-  
 951 liquid extraction because it is generally faster, more efficient, and generates less waste.

952 14.4.5.1 Extraction Chromatography Columns

953 Over the past decade, *extraction chromatography* methods have gained wide acceptance in the  
 954 radiochemistry community as new extraction chromatographic resins have become commercially  
 955 available, such as Sr, TRU, and TEVA resins (Eichrom Industries, Inc., Darien, IL) (Dietz and  
 956 Horwitz, 1993; Horwitz et al., 1991, 1992, and 1993). These resins are composed of extractant  
 957 materials, such as CMPO and 4,4'(5')-bis(t-butylcyclohexano)-18-crown-6, absorbed onto an  
 958 inert polymeric support matrix. They are most frequently used in a column, rather than a batch  
 959 mode.

960 Another example of the advances in the area are use of fibrous discs impregnated with high  
 961 molecular weight chelates, selective for certain nuclides such as Cs, Sr, and Tc (Empore Discs,  
 962 3M Company, and the TEVA Disc, Eichrom Industries, Inc.). Many of the traditional methods  
 963 based upon repetitive precipitations, or solvent extraction in separatory funnels, have been  
 964 replaced by this strategy. This approach allows for the specificity of liquid-liquid extraction with  
 965 the convenience of column chromatography. Numerous papers detailing the determination of  
 966 radionuclides by this technique have been published recently, and examples are cited in Table  
 967 14.6.

968 **TABLE 14.6 — Radioanalytical methods employing extraction chromatography<sup>(1)</sup>**

Analyte	Ligand	Method Citations
Ni-59/63	dimethylgloxime	Aqueous samples (DOE, 1997)
Sr-89/90	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Biological, Environmental, and Nuclear Waste (Horwitz et al., 1991 and 1992); Water (ASTM, D5811-95; DOE, 1995, Method RP500); Urine (Dietz and Horwitz, 1992; Alvarez and Navarro, 1996); Milk (Jeter and Grob, 1994); Geological Materials (Pin and Bassin, 1992)
Sr-90	octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide [CMPO] in tributyl phosphate	Brines (Bunzl et al., 1996)
Y-90	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Medical applications (Dietz and Horwitz, 1992)
Tc-99	Aliquat-336N	Low-level radioactive waste (Banavali, 1995); Water (Sullivan et al., 1993; DOE, 1993, Method RP550)

Analyte	Ligand	Method Citations
975 Pb-210	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in isodecanol	Water (DOE, 1995, Method RP280); Geological materials (Horwitz et al., 1994; Woittiez and Kroon, 1995); complex metal ores (Gale, 1996)
976 Ra-228	octyl(phenyl)- <i>N,N</i> -diisobutyl-carbamoylmethylphosphine oxide [CMPO] in tributyl phosphate or diethylhexyl-phosphoric acid [HDEHP] impregnated in Amberlite XAD-7	Natural waters (Burnett et al., 1995); Volcanic rocks (Chabaux, 1994)
977 Rare earths	diamyl,amylphosphonate  octyl(phenyl)- <i>N,N</i> -diisobutyl-carbamoylmethylphosphine oxide [CMPO] in tributyl phosphate and diethylhexyl-phosphoric acid [HDEHP] impregnated in Amberlite XAD-7  octyl(phenyl)- <i>N,N</i> -diisobutyl-carbamoylmethylphosphine oxide [CMPO] in tributyl phosphate and 4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Actinide-containing matrices (Carney, 1995)  Sequential separation of light rare earths, U, and Th in geological materials (Pin et al., 1996)  Concomitant separation of Sr, Sm, and Nd in silicate samples (Pin et al., 1994)
978 Actinides	octyl(phenyl)- <i>N,N</i> -diisobutyl-carbamoylmethylphosphine oxide [CMPO] in tributyl phosphate  diamyl,amylphosphonate  tri- <i>n</i> -octylphosphine oxide [TOPO] and di(2-ethylhexyl)phosphoric acid [HDEHP]	Air filters (Berne, 1995); Waters (Berne, 1995); Group-screening (DOE, 1997, Method RP725); Urine (Horwitz et al., 1990; Nguyen et al., 1996); Acidic media (Horwitz, 1993; DOE, 1997); Soil and sludge (Smith et al., 1995; Kaye et al., 1995); Environmental (Bunzl and Kracke, 1994)  Acidic media (Horwitz et al., 1992)  Environmental and industrial samples (Testa et al., 1995)

979 (1) This list is representative of the methods found in the literature. It is not complete, nor does it imply preference  
980 over methods not listed.

#### 981 14.4.5.2 Extraction Membranes

982 SPE membranes have also become a popular approach to sample preparation for organic  
983 compounds in aqueous samples over the past decade. As of 1995, 22 methods employing SPE  
984 disks have been accepted by the U.S. Environmental Protection Agency. More recently, disks  
985 have been developed for specific radionuclides, such as technetium, strontium, and radium  
986 (DOE, 1990 and 1997; Orlandini, 1998; Smith et al., 1996 and 1997).

987 These SPE membranes significantly reduce extraction time and reagent use. Samples typically  
988 are processed through the membranes at flow rates of at least 50 milliliters per minute; a one liter  
989 sample can be processed in as little as 20 minutes. Moreover, these selective-membranes often  
990 can be counted directly, thereby condensing sample preparation and counting source preparation  
991 into a single step. Many of the hazardous reagents associated with more traditional methods are  
992 eliminated in this approach, and these membrane-based extractions use up to 90 percent less  
993 solvent than liquid-liquid extractions. The sorbent particles embedded in the membrane are  
994 extremely small and evenly distributed, thereby eliminating the problem of channeling that is  
995 associated with columns.

#### 996 **14.4.6 Advantages and Disadvantages of Solvent Extraction**

##### 997 14.4.6.1 Advantages

- 998 • Lends itself to rapid and very selective separations that are usually highly efficient.
- 999 • Partition coefficients are often approximately independent of concentration down to tracer  
1000 levels and, therefore, can be applied to a wide range of concentrations.
- 1001 • Can usually be followed by back-extraction into aqueous solvents or, in some cases, the  
1002 solution can be used directly in subsequent procedures.
- 1003 • Wide scope of applications—the composition of the organic phase and the nature of  
1004 complexing or binding agents can be varied so that the number of practical combinations is  
1005 virtually unlimited.
- 1006 • Can be performed with simple equipment, but can also be automated.
- 1007 • Column extraction is fast, very selective, generates a low volume of waste, can often be  
1008 applied to samples from very acidic media, requires relatively inexpensive materials, and can  
1009 often be correlated with liquid/liquid extraction.

##### 1010 14.4.6.2 Disadvantages

- 1011 • Cumbersome for a large number of samples or for large samples.
- 1012 • Often requires toxic and/or flammable solvents.

- 1013 • Can be time consuming, especially if attainment of equilibrium is slow.
- 1014 • Can require costly amounts of organic solvents and generate large volumes of organic waste.
- 1015 • Can be affected by small impurities in the solvent(s).
- 1016 • Multiple extractions might be required, thereby increasing time, consumption of materials,  
1017 and generation of waste.
- 1018 • Formation of emulsions can interfere.
- 1019 • Counter-current process can be complicated and can require complicated equipment.
- 1020 • Alteration of chemical form can change, going from one phase to the other, thereby altering  
1021 the distribution coefficient and effectiveness of the extraction.
- 1022 • Tracer-levels of analytes can form radiocolloids that cannot be extracted, dissociate into less  
1023 soluble forms, or adsorb on the container surface or onto impurities in the system.
- 1024 • Extraction columns cannot be reused.

## 1025 **14.5 Volatilization and Distillation**

### 1026 **14.5.1 Introduction**

1027 Differences in vapor pressures of elements or their compounds can be exploited for the  
1028 separation of radionuclides. Friedlander et al. (1981, p. 300), describes the process:

1029 “The most straightforward application is the removal of radioactive rare gases from aqueous  
1030 solutions or melts by sweeping an inert gas or helium. The volatility of ... compounds ... can  
1031 be used to effect separations ...by distillation ... Distillation and volatilization methods often  
1032 give clean separations, provided that proper precautions are taken to avoid contamination of  
1033 the distillate by spray or mechanical entrapment. Most volatilization methods can be done  
1034 without specific carriers, but some nonisotopic carrier gas might be required. Precautions are  
1035 sometimes necessary to avoid loss of volatile radioactive substances during the dissolving of  
1036 irradiated targets or during irradiation itself.”

1037 Similar precautions are also advisable during the solubilization of samples containing volatile  
1038 elements or compounds (Chapter 13, *Sample Dissolution*).

### 1039 **14.5.2 Volatilization Principles**

1040 Volatilization particularly provides a rapid and often selective method of separation for a wide  
1041 range of elements (McMillan, 1975, p. 306). A list of the elements that can be separated by  
1042 volatilization and their chemical form(s) upon separation are given in Table 14.7 (McMillan,  
1043 1975, p. 307).

1044 McMillan continues (1975, p. 306):

1045 “While many of the volatile species are commonly encountered and a large proportion can be  
1046 produced from aqueous solutions, a significant number are rarely met. The volatilization of  
1047 highly reactive materials and those with high boiling points are only used in special  
1048 circumstances, e.g., for very rapid separations. ... Many other volatile compounds have been  
1049 used to separate the elements, including sulphides, carbonyls, stable organic complexes ... ,  
1050 and fluorinated  $\beta$ -diketones for the lanthanides.”

1051 “Separation, ... , is achieved by differentiation during the volatilization process, fractionation  
1052 by transfer, and selective collection. Gaseous evolution can be controlled by making use of  
1053 differences in vapor pressure with temperature, adjustment of the oxidation state of the  
1054 element in solution or by alteration of the matrix, in order to change the chemical  
1055 combination of the element. Once gaseous, additional separation is possible and physical  
1056 processes can be adopted such as gas chromatography, zone refining, fractional distillation,  
1057 electrostatic precipitation, filtration of condensed phases and low temperature trapping.  
1058 Chemical methods used are mainly based on the selective trapping of interfering substances  
1059 by solid or liquid reagents. The methods of preferential collection of the species sought are  
1060 similar to those used in the transfer stage.”Both solid and liquid samples can be used in  
1061 volatilization separations (Krivan, 1986, p. 377):

1062 “With solid samples, there are several types of separation methods. The most important of  
1063 them are ones in which (1) the gas forms a volatile compound with only the trace elements  
1064 and not the matrix, (2) the gas forms a volatile compound with the matrix but not the trace  
1065 elements, and (3) volatile compounds are formed with both the matrix and the trace elements.  
1066 Different gases have been used in separation by volatilization, including inert gases  $N_2$ , He,  
1067 and Ar and the reactive gases  $H_2O$ ,  $O_2$ ,  $H_2$ , ...  $F_2$ , and HF. The apparatus usually consists of



1068 three parts: gas regulation and purification, oven with temperature programming and control,  
1069 and condensation or adsorption with temperature regulation.”

1070 “The radiotracer technique provides the best way to determine the recoveries of trace  
1071 elements in the volatilization process and to optimize the separation with respect to the  
1072 pertinent experimental parameters.”

### 1073 **14.5.3 Distillation Principles**

1074 *Distillation* is the separation of a volatile component(s) of a mixture by vaporization at the  
1075 boiling point of the mixture and subsequent condensation of the vapor. The vapor produced on  
1076 boiling the mixture is richer in the more volatile component—the component with the higher  
1077 vapor pressure (partial pressure) and correspondingly lower boiling point. The process of  
1078 distillation, therefore, essentially takes advantage of the differences in the boiling points of the  
1079 constituents to separate a mixture into its components. It is a useful separation tool if the analyte  
1080 is volatile or can be transformed into a volatile compound. Most inorganic applications of  
1081 distillation involve batch distillation, whereas most organic applications require some type of  
1082 fractional distillation. In a simple batch distillation, the sample solution containing a single  
1083 volatile component or components with widely separated boiling points is placed in a distillation  
1084 flask, boiling is initiated, and the vapors are then continuously removed, condensed, and  
1085 collected. Mixtures containing multiple volatile components require *fractional distillation*, which  
1086 employs repeated vaporization-condensation cycles for separation, and is commonly performed  
1087 in a *fractionation column* for that purpose. The column allows the cycles to occur in one  
1088 operation, and the separated component is collected after the last condensation.

1089 Distillation has been widely used for separating organic mixtures but this approach has less  
1090 applicability in inorganic analysis (Korkisch, 1969, p. 25). Korkisch states: “Nevertheless, some  
1091 of the elements of interest to radiochemists can be very effectively separated by distillation as  
1092 their volatile chlorides, bromides, and oxides .... these elements are germanium (Ge), selenium  
1093 (Se), technetium (Tc), rhenium (Re), ruthenium (Ru), and osmium (Os) (Korkisch, 1969, p. 25;  
1094 also see DOE, 1995 Method RP530). Two common analytes determined through distillation,  
1095 tritium and <sup>226</sup>Ra, by radon emanation are discussed below.

1096 Specific distillation principles are commonly found in chemistry reference and textbooks. For a  
1097 theoretical discussion of distillation see Peters (1974) and Perry and Weisberger (1965, pp. 1-  
1098 229). Distillation procedures are discussed for many inorganic applications in Dean (1995) and  
1099 for less common radioanalytes in the NAS-NS 3108 Monograph, *Application of Distillation*

1100 *Techniques to Radiochemical Separation* (DeVoe, 1962), and in NAS-NS 3104 Monograph,  
1101 *Rapid Radiochemical Separations* (Kuska and Meinke, 1961).

#### 1102 **14.5.4 Separations in Radiochemical Analysis**

1103 The best known use of distillation in radiochemical analysis is in the determination of tritium  
1104 (EPA, 1984, pp. H-01-1-8; DOE, 1995, pp. RP580). Water is the carrier as simple distillation is  
1105 used to separate tritium from water or soil samples. For determination of tritium, the aqueous  
1106 sample is treated with a small amount of sodium hydroxide (NaOH) and potassium permanganate  
1107 ( $\text{KMnO}_4$ ), and it is then distilled. The early distillate is discarded, and a portion of the distillate is  
1108 collected for tritium determination by liquid scintillation counting. The alkaline treatment  
1109 prevents other radionuclides, such as radioiodine or radiocarbon, from distilling over with the  
1110 tritium ( $^3\text{H}$ ), and the permanganate ( $\text{MnO}_4^{-1}$ ) treatment destroys trace organic material in the  
1111 sample that could cause quenching during the counting procedure.

1112 Larger samples are distilled using a round-bottom flask, while a MICRO DIST<sup>®</sup> tube can be  
1113 utilized for smaller samples (DOE, 1995, Method RP580). The distillate can be added directly to  
1114 a liquid scintillation cocktail (EPA, 1980, Method 906.0), or further enriched by acid electrolysis  
1115 (DOE, 1990 and 1997, Method  $^3\text{H}$ -01) or alkaline electrolysis (DOE, 1990 and 1997, Method  $^3\text{H}$ -  
1116 02).

1117 Iodine ( $\text{I}_2$ ) is separated from aqueous samples by distillation from acidic solutions into alkaline  
1118 solutions (EPA, 1973, pp. 73-76). Iodide ( $\text{I}^{-1}$ ) is added as carrier; but nitric acid ( $\text{HNO}_3$ ) as part of  
1119 the acid solution, oxidizes the anion to molecular iodine as the mixture is heated for distillation.

1120 One determination of  $^{79}\text{Se}$  employs an optional purification step, distillation of the metal as  
1121 selenous acid,  $\text{H}_2\text{SeO}_3$  (DOE, 1995, Method RP530). The solution is maintained with excess  
1122 bromine ( $\text{Br}_2$ ) and hydrobromic acid (HBr) to hold the selenium in the oxyacid form during the  
1123 distillation. Technetium can be separated from other elements, or can be separated from  
1124 ruthenium, osmium, or rhenium by distillation of their oxides (Friedlander et al., 1981, p 300).  
1125 Metals are sometimes distilled in their elemental form—polonium in bismuth or lead (McMillan,  
1126 1975, p. 308).

1127  $^{226}\text{Ra}$  in solution can be determined by de-emanating its gaseous progeny  $^{222}\text{Rn}$  into an ionization  
1128 chamber or scintillation cell. Generally, the procedure initially involves the concentration of  
1129 radium by coprecipitation with barium sulfate ( $\text{BaSO}_4$ ). The barium sulfate is then dissolved in  
1130 an EDTA solution, transferred to a sealed bubbler, and stored to allow for the ingrowth of  $^{222}\text{Rn}$ .  
1131 Following sufficient in-growth, the  $^{222}\text{Rn}$  is de-emanated by purging the solution with an inert

1132 gas, such as helium (He) or argon (Ar), and is transferred via a drying tube to a scintillation cell  
1133 or ionization chamber. After the short-lived  $^{222}\text{Rn}$  progeny have reached secular equilibrium with  
1134 the  $^{222}\text{Rn}$  (approximately four hours), the sample is counted to determine alpha activity (EPA,  
1135 1980, Method 903.1; DOE, 1990 and 1997, Methods Ra-01 through Ra-07; Sedlet, 1966; Lucas,  
1136 1990).

1137 When processing samples containing radon, care should be taken to guard against the inadvertent  
1138 loss of the gas or contamination of the distillation apparatus. Radon can be adsorbed on, or  
1139 permeate through, materials used in its handling. Diffusion through rubber and plastic tubing or  
1140 through polyethylene bottles has been observed. Since radon is soluble in many organic  
1141 compounds, impurities, including greases used in ground-glass connections, can increase  
1142 adsorption.

#### 1143 **14.5.5 Advantages and Disadvantages of Volatilization**

##### 1144 14.5.5.1 Advantages

- 1145 • Can be very selective, producing clean separations.
- 1146 • Very rapid, especially with high-vacuum equipment.
- 1147 • Can be performed from solid or liquid samples.
- 1148 • Most can be performed without a specific carrier gas.

##### 1149 14.5.5.2 Disadvantages

- 1150 • Relatively few volatile elements or inorganic compounds are available.
- 1151 • Atmosphere can alter the nature of a volatile form of the tracer or surface material.
- 1152 • Effects of experimental parameters (carrier gas, gas flow, temperature, time, and recovery)  
1153 are highly variable.
- 1154 • Precautions are sometimes necessary to avoid loss of volatile radionuclide substances during  
1155 subsequent procedures.
- 1156 • Some systems require high-temperature, complex equipment.
- 1157 • Contamination of distillate by carrier, spray, or mechanical entrapment is a potential problem.

1158 **14.6 Electrodeposition**1159 **14.6.1 Electrodeposition Principles**

1160 Radionuclides in solution as ions can be deposited (plated) by electrochemical reactions (redox  
1161 reactions) onto an electrode, either by a spontaneous process (produced by a favorable electrode  
1162 potential existing between the ion and electrode) or by a nonspontaneous process (requiring the  
1163 application of an external voltage (potential) (Section 14.2, “Oxidation and Reduction  
1164 Processes”).

1165 Spontaneous electrochemical processes are described by the Nernst equation, which relates the  
1166 electrode potential of the reaction to the activity of substances participating in a reaction:

$$1167 \quad E = E^0 - \frac{RT}{nF} \ln(a_p/a_r)$$

1168 where  $E$  is the electrochemical potential,  $E^0$  is the standard potential for the process,  $R$  is the  
1169 ideal gas constant,  $T$  is the absolute temperature,  $n$  is the number of electrons exchanged in the  
1170 redox reaction,  $F$  is Faraday’s constant, and  $a_p$  and  $a_r$  are the activities of the products of the  
1171 reaction and the reactants, respectively. The *activity* ( $a$ ) of ions in solution is a measure of their  
1172 molar concentration ( $c$  in moles/L) under ideal conditions of infinite dilution. Expressing the  
1173 activities in terms of the product of molar concentrations and activity coefficients,  $\gamma$  (a measure  
1174 of the extent the ion deviates from ideal behavior in solution; thus  $a = \gamma \cdot c$ , where  $\gamma \leq 1$ ), the  
1175 Nernst equation becomes:

$$1176 \quad E = E^0 - \frac{RT}{nF} \ln(\gamma_p c_p / \gamma_r c_r)$$

1177 For dilute solutions of electrolytes ( $\leq 10^{-2}$  molar), the activity coefficient is approximately one  
1178 ( $\gamma \approx 1$ ; it approaches one as the solution becomes more dilute, becoming one under ideal  
1179 conditions). Then, the Nernst equation is expressed in terms of the concentrations of ions in  
1180 solution, the typical form in which the equation is found in most chemistry textbooks (see also  
1181 Section 14.8.3.1, “Solubility and Solubility Product Constant,  $K_{sp}$ ,” for an application of activity  
1182 to the solubility product constant):

$$1183 \quad E = E^0 - \frac{RT}{nF} \ln(c_p/c_r)$$

1184 At concentrations less than  $10^{-6}$ M, electrodeposition may show considerable deviations from  
1185 behavior of macroamounts of elements whose behavior partly depends on the nature and  
1186 previous treatment of the electrode (Adolff and Guillaumont, 1993, p. 275). Inconsistent

1187 behavior is the result of heterogeneity of the surface metal, a very important consideration when  
1188 electrodepositing radionuclides at very low concentrations. The spontaneity predicted by the  
1189 Nernst equation for macroconcentrations of ions in solution at controlled potential is not always  
1190 observed for microconcentrations (Choppin et al., 1995, p. 246). The activity of radionuclide ions  
1191 is usually unknown at low concentrations even if the concentration is known, because the activity  
1192 coefficient ( $\gamma$ ) is dependent on the behavior of the mixed electrolytic system. In addition, the  
1193 concentration might not be accurately known because ions might adsorb on various surfaces,  
1194 form complexes with impurities, or precipitate on the electrode, for example. (See section  
1195 14.9.3.7, "Oxidation and Reduction of Tracers," for another application of the Nernst equation.)  
1196 Separation is limited partly because electrodeposition from very dilute solutions is slow, but it is  
1197 also limited because it rarely leads to complete separation of one element from many others  
1198 (Coomber, 1975, p. 313). Overall, the behavior of an element during an electrochemical process  
1199 is determined by its electrochemical potential, which depends on the nature of the ion; its  
1200 chemical form, its concentration, the general composition of the electrolyte, the current density,  
1201 material and design of the electrode, and construction features of the electrochemical cell  
1202 (Zolotov, 1990, pp. 94-95).

1203 Often trace elements are deposited on a solid cathode, but large separation factors between  
1204 micro- and macro-components are required. This condition is met when electrochemically active  
1205 metals are the main components or when the analyzed matrix does not contain macro-  
1206 components that will separate on the cathode (Zolotov, 1990, p. 95). Deposition of heavy metals  
1207 and actinides can be more difficult to control, for example, because of the decomposition of  
1208 water and reactions of cations and anions at electrodes (Adolff and Guillaumont, 1993, p. 158).  
1209 In some cases, deposition of matrix components can be avoided by selection of a suitable  
1210 medium and composition of the electrolyte. Overall, the effectiveness of electrodeposition of  
1211 trace components depends on the electrode potential, electrode material and its working surface  
1212 area, duration of electrolysis, properties of the electrolyte (composition and viscosity),  
1213 temperature, and mixing rate (Zolotov, 1990, pp. 95-96). Even so, published data are empirical  
1214 for the most part, and conditions for qualitative reproducible separation are determined for each  
1215 case. It is difficult, therefore, to make general recommendations for selecting concentration  
1216 conditions. It is advisable to estimate and account for possible effects of different electrolysis  
1217 factors when developing separation or concentration methodologies (Zolotov, 1990, p. 98).

#### 1218 **14.6.2 Separation of Radionuclides**

1219 Although electrodeposition is not frequently used as a radiochemical separation technique,  
1220 several radionuclides [including iron (Fe) (Hahn, 1945), cadmium (Cd) (Wright, 1947), and  
1221 technetium (Tc) (Flagg, 1945)] have been isolated by electrodeposition on a metal electrode.

1222 Electrodeposition is, however, the standard separation technique for polonium (Po), copper (Cu),  
1223 and platinum (Pt). Polonium is isolated through deposition on nickel from a strong hydrochloric  
1224 acid (HCl) medium (DOE, 1990 and 1997, Method Po-01). This separation is very specific, and,  
1225 therefore, can be accomplished in the presence of many other radionuclides. Electrodeposition at  
1226 a mercury cathode has also been used to separate technetium from fission products and for group  
1227 separation of fission products (Coomber, 1975, p. 198). Numerous metals have been deposited  
1228 on thin metal films by electrolysis with a magnesium (Mg) cathode. According to Coomber,  
1229 “Electrodeposition of metals can be sensitive to the presence of other substances” (Coomber,  
1230 1975, p. 198). Deposition of polonium on silver (Ag) is inhibited by iron unless a reducing agent  
1231 is present; and the presence of fluoride ( $F^{-1}$ ), trace amounts of rare earths, can inhibit the  
1232 deposition of americium (Am). “In many cases the uncertainties of yield can be corrected by the  
1233 use of another radioisotope as an internal standard” (Coomber, 1975, p. 198).

### 1234 14.6.3 Preparation of Counting Sources

1235 Electrodeposition is primarily used to prepare counting sources by depositing materials uniformly  
1236 in an extremely thin layer. Because of potential self-absorption effects, this approach is ideal for  
1237 the preparation of alpha sources. Numerous methods have been published for the electro-  
1238 deposition of the heavy metals, e.g., the Mitchell method from hydrochloric acid (Mitchell,  
1239 1960), the Talvitie method from dilute ammonium sulfate  $[(NH_4)_2SO_4]$  (Talvitie, 1972), and the  
1240 Kressin method from sodium sulfate-sodium bisulfate media (Kressin, 1977).

1241 Sill and Williams (1981) and Hindman (1983, 1986) contend that coprecipitation is the preferred  
1242 method for preparation of sources for alpha spectrometry and that it should be assessed when  
1243 electrodeposition is being considered. Also see Section 16.7.2, “Coprecipitation,” in this manual.

### 1244 14.6.4 Advantages and Disadvantages of Electrodeposition

#### 1245 14.6.4.1 Advantages

- 1246 • Highly selective in some cases.
- 1247 • Deposits material in an extremely thin uniform layer resulting in excellent spectral resolution.
- 1248 • One of the common methods for preparing actinides for alpha spectrometry.

#### 1249 14.6.4.2 Disadvantages

- 1250 • Not applicable to many radionuclides.

- 1251
- Sensitive to the presence of other substances.
- 1252
- For tracer-level quantities, the process is relatively slow, it seldom leads to complete
- 1253
- separation of one element from many others, and there is usually no direct comparison of
- 1254
- concentration in solution to deposited activity.
- 1255
- No further separations can be performed (see Section 16.7.2, “Coprecipitation,” for methods
- 1256
- using  $\text{NdF}_3$ ).

## 1257 **14.7 Chromatography**

### 1258 **14.7.1 Chromatographic Principles**

1259 *Chromatography* is a separation technique that is based on the unequal distribution (partition) of  
1260 substances between two immiscible phases, one moving past the other. A mixture of the  
1261 substances (the analytical mixture) in the *mobile* phase passes over the *immobile phase*. Either  
1262 phase can be a solid, liquid, or gas, but the alternate phase cannot be in the same physical state.  
1263 The two most common phase pairs are liquid/solid and gas/liquid. Separation occurs as the  
1264 components in the mixture partition between the two phases because, in a properly designed  
1265 chromatographic system, the phases are chosen so that the distribution of the components  
1266 between the phases is not equal.

1267 With the broad range of choices of phase materials, the number of techniques employed to  
1268 establish differential distributions of components between the phases, and the various practical  
1269 laboratory methods used to cause the mobile phases to pass over the immobile phases, there are  
1270 many chromatographic techniques available in separation chemistry. The names of the  
1271 chromatographic techniques themselves partially identify the methods or principles employed  
1272 and suggest the variety of applications available using this approach to separation. They include  
1273 paper chromatography, ion-exchange chromatography, adsorption chromatography, gas  
1274 chromatography, high-pressure liquid chromatography, and affinity chromatography. Each aspect  
1275 of chromatography used in separation chemistry will be described below, including the phases  
1276 commonly employed, the principles used to establish differential distributions, and the laboratory  
1277 techniques employed to run a chromatographic separation.

1278 The most common phase pairs used in chromatography are a mobile liquid phase in contact with  
1279 a solid phase. The liquid phase can be a pure liquid, such as water or an organic solvent, or it can  
1280 be a solution, such as methyl alcohol, sodium chloride in water, or hexane in toluene. The solid  
1281 phase can be a continuous material such as paper, or a fine-grained solid such as silica, powdered

1282 charcoal, or alumina. The fine-grained solid can also be applied to a supporting material, such as  
1283 paper, plastic, or glass, to form a coat of continuous material. Alternatively, gas/liquid phase  
1284 systems can consist of an inert gas, such as nitrogen (N<sub>2</sub>) or helium (He), in conjunction with a  
1285 high-boiling point liquid polymer coated on the surface of a fine-grained inert material, such as  
1286 firebrick. This system is called *gas-liquid phase chromatography (GLPC)*, or simply *gas*  
1287 *chromatography (GC)*. In each system, both phases play a role in the separation by offering a  
1288 physical or chemical characteristic that will result in differential distribution of the components  
1289 of the analytical mixture being separated. Liquid/liquid phase systems are similar to gas/liquid  
1290 phase systems in that one of the liquid phases is bound to an inert surface and remains stationary.  
1291 These systems are often referred to as *liquid partition chromatography* or *liquid-phase*  
1292 *chromatography (LPC)*, because they are essentially liquid-liquid extraction systems with one  
1293 mobile and one immobile phase (Section 14.4, “Solvent Extraction”).

1294 Differential distributions are established between the separating phases by the combination of  
1295 physical and chemical properties of the two phases in combination with those of the components  
1296 of the analytical mixture. The properties that are most commonly exploited by separation  
1297 chromatography are solubility, adsorption, ionic interactions, complementary interactions, and  
1298 selective inclusion. One or more of these properties is acting to cause the separation to occur.

#### 1299 **14.7.2 Gas-Liquid and Liquid-Liquid Phase Chromatography**

1300 In gas-liquid phase chromatography, the components of the analytical mixture are first converted  
1301 to a vapor themselves and added to the flowing gas phase. They are then partitioned between the  
1302 *carrier gas* and liquid phases primarily by solubility differences of the components in the liquid  
1303 phase. As the gas/vapor mixture travels over the liquid phase, the more soluble components of  
1304 the mixture spend more time in the liquid. They travel more slowly through the chromatography  
1305 system and are separated from the less soluble, and therefore faster moving, components.  
1306 Liquid/liquid phase chromatography provides separation based on the same principle of  
1307 solubility in the two liquid phases, but the separation is performed at ambient temperatures with  
1308 the components of the analytical mixture initially dissolved in the mobile phase. Partitioning  
1309 occurs between the two phases as the mobile phase passes over the stationary liquid phase.

1310 Gas chromatography has been used to concentrate tritium, and to separate krypton and xenon  
1311 fission products and fission-produced halogens (Coomber, 1975, p. 189). A large number of  
1312 volatile metal compounds could be separated by gas chromatography, but few have been  
1313 prepared. Lanthanides and trivalent actinides have been separated on glass capillary columns  
1314 using volatile double halides formed with aluminum chloride (Coomber, 1975, p. 189).

1315 **14.7.3 Adsorption Chromatography**

1316 *Adsorption chromatography* partitions components of a mixture by means of their different  
1317 adsorption characteristics onto the surface of a solid phase and their different solubilities in a  
1318 liquid phase. Adsorption phenomena are primarily based on intermolecular interactions between  
1319 the chemical components on the surface of the solid and the individual components of the  
1320 mixture. They include Van der Waals forces, dipole-dipole interactions, and hydrogen bonds.  
1321 Silica is a useful adsorption medium because of the ability of its silyl OH groups to hydrogen  
1322 bond or form dipole-dipole interactions with molecules in the mixture. These forces compete  
1323 with similar intermolecular interactions—between the liquid phase and the components of the  
1324 mixture—to produce the differential distribution of the components. This process causes  
1325 separation to occur as the liquid phase passes over the solid phase.

1326 Many separations have been performed via paper and thin-layer chromatography. Modified and  
1327 treated papers have been used to separate the various valence states of technetium (Coomber,  
1328 1975, p. 189).

1329 **14.7.4 Ion-Exchange Chromatography**

1330 14.7.4.1 Principles of Ion Exchange

1331 Since the discovery by Adams and Holmes (1935) that synthetic resins can have ion-exchanging  
1332 properties, ion exchange has become one of the most popular, predominant, and useful tech-  
1333 niques for radiochemical separations, both with and without carriers. There are many excellent  
1334 references available in the literature, e.g., Dean (1995), Dorfner (1972), Korkisch (1989), Rieman  
1335 and Walton (1970), and NAS monographs (listed in References, under the author's name). The  
1336 journal, *Ion Exchange and Solvent Extraction*, reports recent advances in this field of separation.

1337 Ion-exchange methods are based on the reversible exchange of metal ions between a liquid  
1338 phase, typically water, and a solid ionic phase of opposite charge, the *resin*. The resin competes  
1339 with the ion-solvent interactions in the liquid phase, primarily ion-dipole interactions and  
1340 hydrogen bonding, to produce the selective partition of ions, causing separation. The solid phase  
1341 consists of an insoluble, but permeable, inert polymeric *matrix* that contains fixed charged groups  
1342 (exchange sites) associated with mobile counter-ions of opposite charge. It is these counter-ions  
1343 that are exchanged for other ions in the liquid phase. Resins are either naturally occurring sub-  
1344 stances, such as zeolites (inorganic silicate polymers) or synthetic polymers. The synthetic resins  
1345 are organic polymers with groups containing the exchange sites. The *exchange sites* are acid or  
1346 base groups (amines, phenols, and carboxylic or sulfonic acids) used over a specific pH range

1347 where they are in their ionic form. Typical exchange groups for cations ( $K^{+1}$ ,  $Ca^{+2}$ , and  $UO_2^{+2}$ ) are  
 1348 the sulfonate anion,  $RSO_3^{-1}$ , or the carboxylate anion,  $RCOO^{-1}$ . The quaternary-amine cation,  
 1349  $RNH_3^{+1}$ , or its derivative, is a common exchange group for anions ( $Cl^{-1}$ ,  $OH^{-1}$ , and  $UO_2(SO_4)_3^{-4}$ ).

1350 In a practical description of ion-exchange equilibria, the *weight distribution coefficient*,  $K_d$ , and  
 1351 the *separation factor*,  $\alpha$ , are significant. The weight distribution coefficient is defined as:

1352 
$$K_d = (C_1/g_{\text{resin}}) / (C_2 /mL_{\text{solution}})$$

1353 where  $C_1$  is the weight of metal ion adsorbed on 1 g of the dry resin, and  $C_2$  is the weight of  
 1354 metal that remains in 1 mL of solution after equilibrium has been reached. The separation factor  
 1355 refers to the ratio of the distribution coefficients for two ions that were determined under  
 1356 identical experimental conditions:

1357 
$$\text{Separation factor } (\alpha) = K_{d, a} / K_{d, b}$$

1358 where  $a$  and  $b$  refer to a pair of ions. This ratio determines the separability of the two ions;  
 1359 separation will only be achieved if  $\alpha \neq 1$ . The more that  $\alpha$  deviates from unity, the easier it will  
 1360 be to obtain separation.

1361 An example of the separation process is the cation-exchange resin. It is usually prepared for  
 1362 separation procedures as a hydrogen salt of the exchange group. Separation occurs when an  
 1363 aqueous solution of another alkali-metal ion (i.e.,  $Li^{+1}$ ,  $K^{+1}$ ,  $Rb^{+1}$ , or  $Cs^{+1}$ ) comes in contact with  
 1364 the resin. Different ions bond selectively to the exchange group, depending on the separation  
 1365 conditions, displacing the counter-ion that is present in the prepared resin as follows:



1367 Diffusion is an important process during ion exchange; the solute ions must penetrate the pores  
 1368 of the spherical resin beads to exchange with the existing ions. Equilibrium is established  
 1369 between each ion in the analyte solution and the exchange site on the resin. The ion least tightly  
 1370 bonded to the exchange site and most solvated in solution spends more time in solution. Selec-  
 1371 tive bonding is a factor of the size and charge of the ion, the nature of the exchange group, and  
 1372 the pH and ionic strength of the media. The order of strength of bonding at low acid concentra-  
 1373 tions in this example is  $H^{+1}$  or  $Li^{+1} < Na^{+1} < K^{+1} < Rb^{+1} < Cs^{+1}$  (Showsmith, 1984). Under the  
 1374 appropriate conditions, for example,  $Cs^{+1}$  will bond exclusively, or  $Cs^{+1}$  and  $Rb^{+1}$  will bond,  
 1375 leaving the remaining cations in solution. The process can be operated as a batch operation or via  
 1376 continuous-flow with the resin in an ion-exchange column. In either case, actual separation is

1377 achieved as the equilibrated solution elutes from the resin, leaving select ions bonded to the resin  
1378 and others in solution. The ion that spends more time in solution elutes first. The ability to “hold”  
1379 ionic material is the resin capacity, measured in units of mg or meq per gram of resin. Eventually,  
1380 most of the exchange groups are occupied by select ions. The resin is essentially saturated, and  
1381 additional cations cannot bond. In a continuous-flow process, *breakthrough* will then occur. At  
1382 this time, added quantities of select cations ( $\text{Cs}^{+1}$  or  $\text{Cs}^{+1}$  and  $\text{Rb}^{+1}$  in this example) will pass  
1383 through the ion-exchange column and appear in the output solution (*eluate*). No further separa-  
1384 tion can occur after breakthrough, and the bonded ions must be remove to prepare the column for  
1385 additional separation. The number of bed volumes of incoming solution (*eluant*) that passes  
1386 through a column resin before breakthrough occurs provides one relative measure of the treat-  
1387 ment capacity of the resin under the conditions of column use. The bonded cations are displaced  
1388 by adjusting the pH of the medium to change the net charge on the exchange groups. This change  
1389 alters the ability of the exchange groups to attract ions, thereby replacing the bonded cations with  
1390 cations that bond more strongly. More commonly, the resin is treated with a more concentrated  
1391 solution of the counter-ion— $\text{H}^{+1}$  in this example. Excess  $\text{H}^{+1}$  favors the equilibrium that produces  
1392 the initial counter-ion form of the exchange group. This process that returns the column to its  
1393 original form is referred to as “regeneration.”

1394 Overall, selectivity of the exchange resin determines the efficiency of adsorption of the analyte  
1395 from solution, the ease with which the ions can be subsequently removed from the resin, and the  
1396 degree to which two different ions of like charge can be separated from each other. The  
1397 equilibrium distribution of ions between the resin and solution depends on many factors, of  
1398 which the most important are the nature of the exchanging ions, the resin, and the solution:

- 1399 • In dilute solutions, the stationary phase will show preference for ions of higher charge.
- 1400 • The selectivity of ion exchangers for ions increases with the increase of atomic number  
1401 within the same periodic group, i.e.,  $\text{Li}^{+} < \text{Na}^{+} < \text{K}^{+} < \text{Rb}^{+} < \text{Cs}^{+}$ .
- 1402 • The higher the polarizability and the lower the degree of solvation (favored by low charge  
1403 and large size), the more strongly an ion will be adsorbed.
- 1404 • Resins containing weakly acidic and weakly basic groups are highly selective towards  $\text{H}^{+}$  and  
1405  $\text{OH}^{-}$  ions. Ion-exchange resins that contain groups capable of complex formation with  
1406 particular ions will be more selective towards those ions.
- 1407 • As cross-linking is increased (see discussion of resins below), resins become more selective  
1408 in their behavior towards ions of different sizes.

- 1409 • No variation in the eluent concentration will improve the separation for ions of the same  
1410 charge; however, for ions of different net charges, the separation does depend on the eluent  
1411 concentration.

1412 14.7.4.2 Resins

1413 The most popular ion-exchange resins are polystyrenes cross-linked through divinylbenzene  
1414 (DVB). The percentage of DVB present during polymerization controls the extent of cross-  
1415 linking. Manufacturers indicate the degree of cross-linking by a number following an X, which  
1416 indicates the percentage of DVB used. For instance, AG 1-X8 and AG 1-X2 are 8 percent and 2  
1417 percent cross-linked resins, respectively. As this percentage is increased, the ionic groups effec-  
1418 tively come into closer proximity, resulting in increased selectivity. However, increases in cross-  
1419 linking decrease the diffusion rate in the resin particle. Because diffusion is the rate-controlling  
1420 step in column operations, intermediate cross-linking in the range of 4 to 8 percent is commonly  
1421 used.

1422 Particle diameters of 0.04-0.3 mm (50-400 mesh) are commonly used, but larger particles give  
1423 higher flow rates. Difficult separations can require 200-400 mesh resins. Decreasing the particle  
1424 size reduces the time required for attaining equilibrium; but at the same time, it decreases flow  
1425 rate. When extremely small particle sizes are used, pressure must be applied to the system to  
1426 obtain acceptable flow rates (see discussion of high pressure liquid chromatography in Section  
1427 14.7.7, “Chromatographic Methods”).

1428 Ion-exchange resins are used in batch operations, or more commonly, in column processes in the  
1429 laboratory. Columns can be made in any size desired. The diameter of the column depends on the  
1430 amount of material to be processed, and the length of the column depends primarily on the  
1431 difficulty of separations to be accomplished. Generally, the ratio of column height to diameter  
1432 should be 8:1. Higher ratios lead to reduced flow rate; lower ratios might not provide effective  
1433 separations.

1434 Some other factors should be considered when using ion-exchange resins:

- 1435 • Resins should not be allowed to dry out, especially during analysis. Rehydration of dried  
1436 resins will result in cracking; these resins should not be used.
- 1437 • Non-ionic and weakly ionic solutes may be absorbed (not exchanged) by the resin. These  
1438 materials, if present during analysis, can alter the exchange characteristics of the resin for  
1439 certain ions.

- 1440 • Particulate matter present in the analyte solution may be filtered by the resin. This material  
 1441 will have several undesired effects, such as decreased flow rate, reduced capacity, and  
 1442 ineffective separation.
- 1443 • Organic solvents suspended in the analyte solution from previous separation steps can be  
 1444 adsorbed by the resin creating separation problems.

1445 Ion exchangers are classified as *cationic* or *anionic* (*cation exchangers* or *anion exchangers*,  
 1446 respectively), according to their affinity for negative or positive counter-ions. They are further  
 1447 subdivided into strongly or weakly ionized groups. Most cation exchangers (such as Dowex-50  
 1448 and Amberlite IR-100) contain free sulfonic acid groups, whereas typical anion exchangers (such  
 1449 as AG 1 and Dowex-1) have quaternary amine groups with replaceable hydroxyl ions (see Table  
 1450 14.8).

1451 **TABLE 14.8 — Typical functional groups**  
 1452 **of ion-exchange resins**

Cation Exchangers	Anion Exchangers
- SO <sub>3</sub> H	- NH <sub>2</sub>
- COOH	- NHR
- OH	- NR <sub>2</sub>
- SH	- NR <sub>3</sub> <sup>+</sup>

1453 R=alkyl group

1459 The sulfonate resins are known as *strong acid cation (SAC) resins* because the anion is derived  
 1460 from a strong sulfonic acid (RSO<sub>3</sub>H). Likewise, the carboxylate resins are known as *weak acid*  
 1461 *cation (WAC) resins* because the anion is derived from a weak carboxylic acid (RCOOH). R in  
 1462 the formulas represents the inert matrix. The quaternary-amine cation (RNH<sub>3</sub><sup>+1</sup>) or its derivatives,  
 1463 represents the common exchange group for anions.

1464 Several examples from the literature illustrate the use of ion-exchange chromatography for the  
 1465 separation of radionuclides. Radium is separated from other alkaline-earth cations (Be<sup>+2</sup>, Mg<sup>+2</sup>,  
 1466 Ca<sup>+2</sup>, Sr<sup>+2</sup>, and Ba<sup>+2</sup>) in hydrochloric solutions on sulfonated polystyrene resins (Kirby and  
 1467 Salutsky, 1964, pp. 26-27), or converted to an anionic complex with citrate or EDTA and  
 1468 separated on a quaternary ammonium polystyrene resin (Sedlet, 1966, p. 302).

1469 Anion-exchange resins separate anions by an analogous process beginning with a prepared resin,  
 1470 usually in the chloride form (RNH<sub>3</sub><sup>+1</sup>Cl<sup>-1</sup>), and adding a solution of ions. Anion-exchange

1471 chromatography is used in one step of a procedure to isolate thorium for radioanalysis by alpha  
 1472 counting (EPA, 1984, pp. U/Th-01-1-14). Thorium cations ( $\text{Th}^{+4}$ ) form anionic nitrate complexes  
 1473 that bind to an anion-exchange resin containing the quaternary complex,  $\text{R-CH}_2\text{-N}(\text{CH}_3)_3^{+1}$ . Most  
 1474 metal ion impurities do not form the complex and, as cations, they do not bind to the exchanger,  
 1475 but remain with the liquid phase. Once the impurities are removed, thorium itself is separated  
 1476 from the resin by treatment with hydrochloric acid (HCl) that destroys the nitrate complex,  
 1477 leaving thorium in its +4 state, which will not bind to the anionic exchanger.

1478 A selection of commercially available resins commonly employed in the radiochemistry  
 1479 laboratory is given in Table 14.9.

1480 The behavior of the elements on anion- and cation-exchange resins is effectively summarized for  
 1481 several resins in Faris and Buchanan (Faris and Buchanan, 1964), Kraus and Nelson (Kraus and  
 1482 Nelson, 1956), and Nelson et al. (1964). The behavior in concentrated hydrochloric acid is  
 1483 illustrated for cations on cation-exchange resins in Figure 14.3 (Dorfner, 1972, p. 208) and for  
 1484 cations on anion-exchange resins in Figure 14.4 (Dorfner, 1972, p. 210).

1485 **TABLE 14.9 — Common ion-exchange resins<sup>(1)</sup>**

1486 Resin type & 1487 nominal % 1488 cross-link	Minimum wet capacity $\text{meq} \cdot \text{mL}^{-1}$	Density (nominal) $\text{g} \cdot \text{mL}^{-1}$	Description
1489 Anion-exchange resins — gel type — strongly basic — quaternary ammonium functionality			
1490 Dowex, AG or 1491 Eichrom 1492 1- X 4	1.0	0.70	Strongly basic anion exchanger with S-DVB matrix for separation of organic acids, nucleotides, and other anions. Molecular weight exclusion < 1400.
1493 Dowex, AG or 1494 Eichrom 1495 1- X 8	1.2	0.75	Strongly basic anion exchanger with S-DVB matrix for separation of inorganic and organic anions with molecular weight exclusion < 1000. 100-200 mesh is standard for analytical separations.
1496 Anion-exchange resins — gel type — intermediate basicity			
1497 Bio-Rex 5	1.1	0.70	Intermediate basic anion exchanger with primary tertiary amines on an polyalkylene-amine matrix for separation of organic acids.
1498 Anion-exchange resins — gel type — weakly basic — polyamine functionality			
1499 Dowex or AG 1500 4- X 4	0.8	0.7	Weakly basic anion exchanger with tertiary amines on an acrylic matrix. Suitable for use with high molecular weight organic compounds.
1501 Amberlite 1502 IRA-68	1.6	1.06	Acrylic-DVB with unusually high capacity for large organic molecules.

Separation Techniques

Resin type & nominal % cross-link	Minimum wet capacity meq• mL <sup>-1</sup>	Density (nominal) g• mL <sup>-1</sup>	Description
1503 Cation-exchange resins - gel type - strongly acidic - sulfonic acid functionality			
1504 Dowex, AG or 1505 Eichrom 1506 50W- X4	1.1	0.80	Strongly acidic cation exchanger with S-DVB matrix for separation of amino acids, nucleosides and cations. Molecular weight exclusion is < 1400.
1507 Dowex, AG or 1508 Eichrom 1509 50W- X8	1.7	0.80	Strongly acidic cation exchanger with S-DVB matrix for separation of amino acids, metal cations, and cations. Molecular weight exclusion is < 1000. 100-200 mesh is standard for analytical applications.
1510 Amberlite 1511 IR-120	1.9	1.26	8% styrene-DVB type; high physical stability.
1512 Selective ion-exchange resins			
1513 Duolite GT-73	1.3	1.30	Removal of Ag, Cd, Cu, Hg, and Pb.
1514 Amberlite 1515 IRA-743A	0.6	1.05	Boron-specific.
1516 Amberlite 1517 IRC-718	1.0	1.14	Removal of transition metals.
1518 Chelex <sup>®</sup> 100	0.4	0.65	Weakly acidic chelating resin with S-DVB matrix for heavy metal concentration.
1519 Eichrom 1520 Diphonix <sup>®</sup>			Chelating ion-exchange resin containing geminally substituted diphosphonic groups chemically bonded to a styrenic-based polymer matrix. Extraordinarily strong affinity for actinides in the tetra- and hexavalent oxidation states from highly acidic media.
1521 Anion exchanger — macroreticular type — strongly basic — quaternary ammonium functionality			
1522 AG MP-1	1.0	0.70	Strongly basic macroporous anion exchanger with S-DVB matrix for separation of some enzymes, and anions of radionuclides.
1523 Cation-exchange resin — macroreticular type — sulfonic acid functionality			
1524 AG MP-50	1.5	0.80	Strongly acidic macroporous cation exchanger with S-DVB matrix for separation of cations of radionuclides and other applications.
1525 Microcrystalline exchanger			
1526 AMP-1	4.0		Microcrystalline ammonium molybophosphate with cation exchange capacity of 1.2 meq/g. Selectively adsorbs larger alkali-metal ions from smaller alkali-metal ions, particularly cesium.

1527 (1) Dowex is the trade name for Dow resins; AG and Bio-Rex are the trade names for Bio-Rad Laboratories resins;  
 1528 Amberlite is the trade name of Rohm & Haas resins. MP is the acronym for macroporous resin; S-DVB is the  
 1529 acronym for styrene-divinylbenzene.

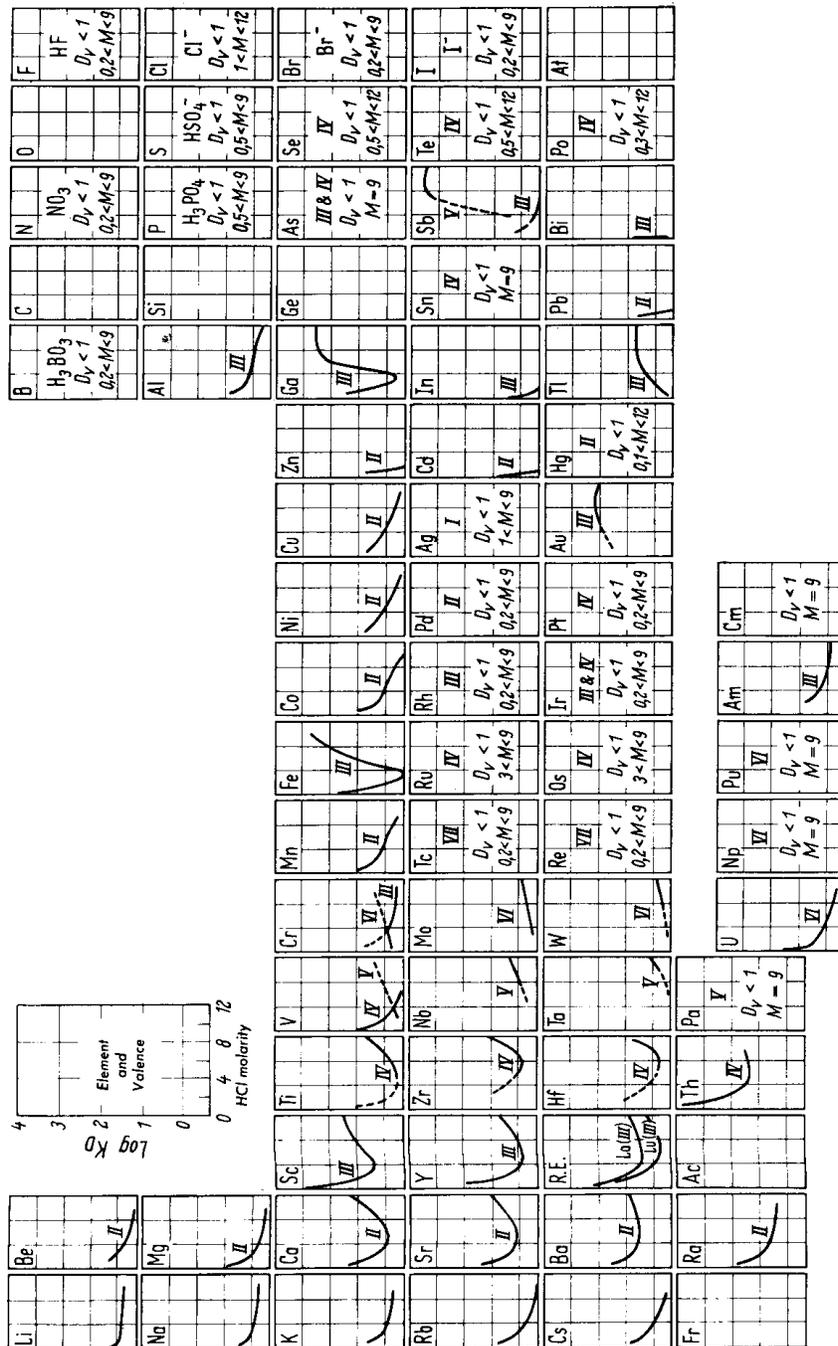


FIGURE 14.3 — The behavior of elements in concentrated hydrochloric acid on cation-exchange resins



1530 **14.7.5 Affinity Chromatography**

1531 Several newer types of chromatography are based on highly selective and specific attractive  
1532 forces that exist between groups chemically bound to an inert solid matrix (ligands) and molecu-  
1533 lar or ionic components of the analytical mixture. Affinity chromatography is an example of this  
1534 separation technique, which is used in biochemistry to isolate antigenic materials, such as  
1535 proteins. The proteins are attracted to their specific antibody that is bonded to a solid matrix.  
1536 These attractive forces are often called complementary interactions because they are based on a  
1537 lock-and-key type of fit between the two constituents. The interaction is complementary because  
1538 the two components match (fit) each other in size and electrical nature.

1539 Crown ethers bonded to solid matrices serve as ligands in a chromatographic separation of  
1540 radium ions from aqueous solutions containing other cations (see Section 14.4.5.1, “Extraction  
1541 Chromatography Columns”). Even other alkaline-earth cations with the same +2 charge, such as  
1542 strontium ( $\text{Sr}^{+2}$ ) and barium ( $\text{Ba}^{+2}$ ), offer little interference with radium binding because the  
1543 cyclic nature of the crown ether creates a ring structure with a cavity that complements the radius  
1544 of the radium ion in solution. In addition, the oxygen atoms of the cyclic ether are inside the ring,  
1545 allowing these electron-dense atoms to form effective ion-dipole interactions through water  
1546 molecules with the radium cation. Radionuclides analyzed by this method include  $^{89}\text{Sr}/^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ ,  
1547  $^{90}\text{Y}$ , and  $^{210}\text{Pb}$ .

1548 **14.7.6 Gel-Filtration Chromatography**

1549 Another physical property that is used to separate molecules by a chromatographic procedure is  
1550 the effective size (molecular weight) of the molecule. High molecular-weight ions can also be  
1551 separated by this procedure. The method is known by several names, including *gel-filtration*  
1552 *chromatography*, *molecular-sieve filtration*, *exclusion chromatography*, and *gel-permeation*  
1553 *chromatography*. This technique is primarily limited to substances such as biomolecules with  
1554 molecular weights greater than 10,000 Daltons. In similar types of solutions (similar solutes and  
1555 similar concentrations), the molecules or ions have a similar shape and molecular weight that is  
1556 approximately proportional to the hydrodynamic diameter (size) of the molecule or ion. The solid  
1557 phase consists of a small-grain inert resin that contains microscopic pores in its matrix that will  
1558 allow molecules and ions up to a certain diameter, called *included particles*, to enter the resin.  
1559 Larger particles are *excluded*. Of the included particles, the smaller ones spend more time in the  
1560 matrices. Separation of the molecules or ions is based on the fact that those substances that are  
1561 excluded are separated in a batch from the included substances, while those that are included are  
1562 separated by size. The log of the molecular weight of the included molecules or ions is  
1563 approximately inversely proportional to the time the particles spend in the matrix.

1564 **14.7.7 Chromatographic Laboratory Methods**

1565 Chromatographic separations are achieved using a variety of laboratory techniques. Some are  
1566 actually quite simple to perform, while others require sophisticated instrumentation. *Paper*  
1567 *chromatography* employs a solid-liquid phase system that separates molecules and ions with  
1568 filter paper or similar material in contact with a developing solvent. The analytical mixture in  
1569 solution is spotted at the bottom of the paper and allowed to dry, leaving the analytes on the  
1570 paper. The paper is suspended so that a small part of the bottom section is in a solvent, but not so  
1571 deep that the dry spots enter the solvent. By capillary action, the solvent travels up the paper. As  
1572 the solvent front moves up, the chromatogram is produced with the components of the mixture  
1573 partitioning between the liquid phase and the paper. *Thin-layer chromatography* is similar, but  
1574 the paper is replaced by a thin solid phase of separatory material (silica gel, alumina, cellulose,  
1575 etc.) coated on an inert support, such as plastic or glass.

1576 *Column chromatography* can accommodate a larger quantity of both phases and can, therefore,  
1577 separate greater quantities of material by accepting larger loads or provide more separating power  
1578 with an increased quantity of solid phase. In the procedure, a solid phase is packed in a glass or  
1579 metal column and a liquid phase is passed through the column under pressure supplied by gravity  
1580 or low-pressure pumping action. For this reason, gravity flow (or pumping the liquid phase under  
1581 pressures similar to those generated by gravity flow) is often referred to as *low-pressure*  
1582 *chromatography*. The liquid phase is usually referred to as the *eluent* and the column is *eluted*  
1583 with the liquid. Column chromatography is the common method used in ion-exchange chroma-  
1584 tography. With column chromatography, separation depends on: (1) type of ion-exchange resin  
1585 used (i.e., cationic, anionic, strong, or weak); (2) eluting solution (its polarity affects ion  
1586 solubility, ionic strength affects displacement of separating ions, and pH affects net charge of  
1587 exchange groups or their degree of ionization in solution); (3) flow rate, grain size, and  
1588 temperature, which affect how closely equilibrium is approached (generally, low flow rate, small  
1589 grain size, and high temperature aid the approach to equilibrium and, therefore, increase the  
1590 degree of separation); and (4) column dimensions (larger diameter increases column capacity,  
1591 while increased length increases separation efficiency by increasing distance between ion bands  
1592 as they travel through the column) (Wahl and Bonner, 1951, pp.137-139).

1593 Metal columns can withstand considerably more pressure than glass columns. *High-pressure*  
1594 *liquid chromatography* (HPLC) employs stainless steel columns and solid phases designed to  
1595 withstand high pressures without collapsing. The method is noted for its rapid separation times  
1596 because of relatively high flow rates under high pressures (up to 2,000 lbs/in<sup>2</sup>). For this reason,  
1597 the acronym HPLC alternatively represents *high-performance liquid chromatography*. HPLC is  
1598 often performed with a liquid-partition technique between an aqueous phase and organic phase,

1599 but gel filtration, ion exchange, and adsorption methods are also employed. In the case of liquid-  
 1600 partition separations, either a stationary aqueous phase or stationary organic phase is selected.  
 1601 The former system is referred to as normal phase chromatography and the latter as reversed phase  
 1602 chromatography, a holdover from the first applications of the technique that employed a  
 1603 stationary aqueous phase. The aqueous phase is made stationary by adsorption onto a solid  
 1604 support, commonly silica gel, cellulose powder, or polyacrylamide. An organic stationary phase  
 1605 is made from particles of a polymer such as polyvinyl chloride or Teflon<sup>®</sup>. Reversed phase HPLC  
 1606 has been used to separate individual elements of the lanthanides and actinides and  
 1607 macroquantities of actinides (Choppin et al., 1995, p. 248).

1608 Gas/liquid phase systems are also used. During gas-liquid phase chromatography (GLPC) [or  
 1609 simply, gas chromatography (GC)], the gas phase flows over the liquid phase (coated onto an  
 1610 inert solid) as an inert carrier gas—commonly helium (He) or nitrogen (N<sub>2</sub>)—flows through the  
 1611 system at low pressure. The carrier gas is supplied from a tank of the stored gas.

#### 1612 **14.7.8 Advantages and Disadvantages of Chromatographic Systems**

1613 Ion-exchange chromatography is by far the predominant chromatographic method used for the  
 1614 separation of radionuclides. Its advantages and disadvantages is presented exclusively in this  
 1615 section.

##### 1616 **Advantages**

- 1617 • Highly selective.
- 1618 • Highly efficient as a preconcentration method.
- 1619 • Works as well with carrier-free tracer quantities  
 1620 as with weighable amounts.
- 1621 • Produces a high yield (recovery).
- 1622 • Can separate radionuclides from interfering  
 1623 counter-ions.
- 1624 • Simple process requiring simple equipment.
- 1625 • Wide scope of applications.
- 1626 • Can handle high volumes of sample.

##### Disadvantages

- May require high volume of eluent.
- Usually a relatively slow process, but rapid  
 selective elution processes are known.
- Requires narrow pH control.

## 1627 **14.8 Precipitation and Coprecipitation**

### 1628 **14.8.1 Introduction**

1629 Two of the most common and oldest methods for the separation and purification of ions in  
 1630 radioanalytical chemistry are *precipitation* and *coprecipitation*. Precipitation is used to isolate

1631 and collect a specific radionuclide from other (foreign) ions in solution by forming an insoluble  
1632 compound. Either the radionuclide is precipitated from solution itself, or the foreign ions are  
1633 precipitated, leaving the radionuclide in solution. Sometimes a radionuclide is present in solution  
1634 at sub-micro concentrations, i.e., levels so low that the radionuclide will not form an insoluble  
1635 compound upon addition of a counter-ion. In these cases, the radionuclide can often be brought  
1636 down from solution by coprecipitation, associating it with an insoluble substance that precipitates  
1637 from solution. This phenomenon is especially important in gravimetric analysis and  
1638 radiochemistry. In gravimetric analysis, carrying down of impurities is a problem. For  
1639 radiochemists, coprecipitation is a valuable tool.

#### 1640 **14.8.2 Solutions**

1641 Precipitation and coprecipitation provide an analytical method that is applied to ions in solution.  
1642 *Solutions* are simply homogeneous mixtures (a physical combination of substances), which can  
1643 be solids, liquids, or gases. The components of a solution consist of a *solute* and a *solvent*. The  
1644 solute is generally defined as the substance that is dissolved, and the solvent is the substance that  
1645 dissolves the solute. In an alternative definition, particularly suitable for liquid components when  
1646 it is not clear what is being dissolved or doing the dissolving, the solute is the minor constituent  
1647 and the solvent is the major constituent. In any event, the solute and solvent can consist of any  
1648 combinations of substances, so long as they are soluble in each other. However, in this chapter,  
1649 we are generally referring to aqueous solutions in which a solute is dissolved in water. The terms  
1650 below further describe solutions:

- 1651 • *Solubility* is defined as the concentration of solute in solution that exists in equilibrium with  
1652 an excess of solute; it represents the maximum amount of solute that can dissolve in a given  
1653 amount of the solvent. The general solubilities of many of the major compounds of concern  
1654 are described in Table 14.10.
- 1655 • An *unsaturated solution* is one in which the concentration of the solute is less than the  
1656 solubility. When additional solute is added to an unsaturated solution, it dissolves.
- 1657 • A *saturated solution* is one that is in equilibrium with an excess of the solute. The  
1658 concentration of a saturated solution is equal to the solubility of the solute. When solute is  
1659 added to the saturated solution, no more solute dissolves.
- 1660 • A *supersaturated solution* is a solution in which the concentration of solute is temporarily  
1661 greater than its solubility—an unstable condition. Therefore, when additional solute is added

1662 to a supersaturated solution, solute comes out of solution as solid until the concentration  
1663 decreases to that of the saturated solution.

1664 **TABLE 14.10 — General solubility behavior of some cations of interest** <sup>(1)</sup>

1665 *The Common Cations*

1666  $\text{Na}^{+1}$ ,  $\text{K}^{+1}$ ,  $\text{NH}_4^{+1}$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ ,  
1667  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Ag}^{+1}$ ,  $\text{Cd}^{+2}$ ,  $\text{Sn}^{+2}$ ,  $\text{Hg}_2^{+2}$ ,  $\text{Hg}^{+2}$ , and  $\text{Pb}^{+2}$

1668 There are general rules of solubilities for the common cations found in most basic chemistry  
1669 texts (e.g., Pauling, 1970, p. 453).

1670 Under the class of *mainly soluble substances*:

- 1671 • All nitrates ( $\text{NO}_3^-$ ) are soluble.
- 1672 • All acetates ( $\text{C}_2\text{H}_3\text{O}_2^-$ ) are soluble.
- 1673 • All chlorides ( $\text{Cl}^-$ ), bromides ( $\text{Br}^-$ ), and iodides ( $\text{I}^-$ ) are soluble, except for those of silver,  
1674 mercury, and lead.  $\text{PbCl}_2$  and  $\text{PbBr}_2$  are sparingly soluble in cold water, and more soluble  
1675 in hot water.
- 1676 • All sulfates ( $\text{SO}_4^{-2}$ ) are soluble, except those of barium, strontium, and lead.  $\text{CaSO}_4$ ,  
1677  $\text{Ag}_2\text{SO}_4$ , and  $\text{Hg}_2\text{SO}_4$  are sparingly soluble.
- 1678 • Most salts of sodium (Na), potassium (K), and ammonium ( $\text{NH}_4^+$ ) are soluble. Notable  
1679 exceptions are  $\text{NaSb}(\text{OH})_6$ ,  $\text{K}_3\text{Co}(\text{NO}_2)_6$ ,  $\text{K}_2\text{PtCl}_6$ ,  $(\text{NH}_4)_2\text{PtCl}_6$ , and  $(\text{NH}_4)_3\text{Co}(\text{NO}_2)_6$ .

1680 Under the class of *mainly insoluble substances*:

- 1681 • All hydroxides ( $\text{OH}^{-1}$ ) are insoluble, except those of the alkali metals (Li, Na, K, Rb, and  
1682 Cs), ammonium, and barium (Ba).  $\text{Ca}(\text{OH})_2$  and  $\text{Sr}(\text{OH})_2$  are sparingly soluble.
- 1683 • All normal carbonates ( $\text{CO}_3^{-2}$ ) and phosphates ( $\text{PO}_4^{-3}$ ) are insoluble, except those of the  
1684 alkali metals and ammonium. Many hydrogen carbonates and phosphates are soluble, i.e.,  
1685  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .
- 1686 • All sulfides ( $\text{S}^{-2}$ ), except those of the alkali metals, ammonium, and the alkaline-earth  
1687 metals (Be, Mg, Ca, Sr, Ba, and Ra), are insoluble. Both aluminum- and chromium sulfide  
1688 are hydrolyzed by water, resulting in the precipitation of  $\text{Al}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$ .
- 1689 • Some cations, such as  $\text{Ba}^{+2}$ ,  $\text{Pb}^{+2}$ , and  $\text{Ag}^{+1}$ , form insoluble chromates ( $\text{CrO}_4^{-2}$ ), which can  
1690 be used as a basis for separation.

1691

*Actinide Elements*

1692

The solubility properties of the actinide  $M^{+3}$  ions are similar to those of the tripositive lanthanide ions, while the behavior of the actinide  $M^{+4}$  ions closely resembles that of  $Ce^{+4}$ .

1693

1694

- The *fluorides* ( $F^-$ ), *oxalates* ( $C_2O_4^{2-}$ ), *hydroxides* ( $OH^-$ ), and *phosphates* are insoluble.

1695

- The *nitrates*, *halides* (except *fluorides*), *sulfates*, *perchlorates* ( $ClO_4^-$ ), and *sulfides* are all soluble.

1696

1697

(1) Solubility data for specific compounds can be found in the CRC Handbook of Chemistry and Physics (CRC, 1999) and in the NAS-NS monographs.

1698

1699

### 14.8.3 Precipitation

1700

Precipitation is accomplished by combining a selected ion(s) in solution with a suitable counter-ion in sufficient concentrations to exceed the solubility of the resulting compound and produce a supersaturated solution. Nucleation occurs and growth of the crystalline substance then proceeds in an orderly manner to produce the precipitate (see Section 14.8.3.1, “Solubility and the Solubility Product Constant,  $K_{sp}$ ”). The precipitate is collected from the solvent by a physical method, such as filtration or centrifugation. A cation (such as  $Sr^{+2}$ , for example) will precipitate from an aqueous solution in the presence of a carbonate anion, forming the insoluble compound, strontium carbonate ( $SrCO_3$ ), when sufficient concentrations of each ion are present in solution to exceed the solubility of  $SrCO_3$ . The method is used to isolate and collect strontium from water for radioanalysis (EPA, 1984, pp. Sr-04-1-19).

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A precipitation process should satisfy three main requirements:

1711

- The targeted species should be precipitated quantitatively.

1712

- The resulting precipitate should be in a form suitable for subsequent handling; it should be easily filterable and should not creep.

1713

1714

- If it is used as part of a quantitative scheme, the precipitate should be pure or of known purity at the time of weighing for gravimetric analysis.

1715

1716

Precipitation processes are useful in several different kinds of laboratory operations, particularly gravimetric yield determinations—as a separation technique and for preconcentration—to eliminate interfering ions, or for coprecipitation.

1717

1718

1719 14.8.3.1 Solubility and the Solubility Product Constant,  $K_{sp}$

1720 Chemists routinely face challenges in the laboratory as a result of the phenomenon of solubility.  
 1721 Examples include keeping a dissolved component in solution and coprecipitating a trace-level  
 1722 analyte from solution.

1723 *Solubility equilibrium* refers to the equilibrium that describes a solid dissolving in solution, such  
 1724 as strontium carbonate dissolving in water, for example:

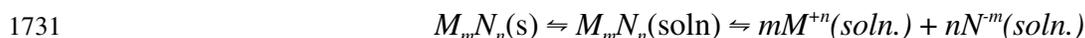


1726 or, alternately, a solid forming from solution, with the carbonate precipitating:



1728 The *solubility product constant*,  $K_{sp}$ , is the equilibrium constant for the former process, a solid  
 1729 dissolving and forming ions in solution. Leussing explains  $K_{sp}$  in general terms as follows:

1730 “For an electrolyte,  $M_mN_n$ , which dissolves and dissociates according to the equation:



1732 “The equilibrium conditions exists that:

1733 
$$a_{MmNn(\text{s})} = a_{MmNn(\text{soln})} = a_{M^{+n}(\text{soln})}^m \cdot a_{N^{-m}(\text{soln.})}^n$$

1734 “[The value  $a$  is the *activity* of the ions in solution, a measure of the molar concentration  
 1735 (moles/L) of an ion in solution under ideal conditions of infinite dilution.] (Also see Section  
 1736 14.6.1, *Principles of Electrodeposition*, for a discussion of activity as applied to the Nernst  
 1737 equation.) [This equation] results in the familiar solubility product expression since the  
 1738 activity of a solid under given conditions is a constant. Expressing the activities in terms of  
 1739 the product of molar concentrations and *activity coefficients*,  $\gamma$  [a measure of the extent the  
 1740 ion deviates from ideal behavior in solution; thus  $a = \gamma \cdot c$  where  $\gamma \leq 1$ ], [this] equation  
 1741 becomes...

1742 
$$[M^{+n}]^m [N^{-m}]^n \gamma_{M^{+n}}^m \gamma_{N^{-m}}^n = \text{a constant} = K_{sp}$$

1743 (Leussing, 1959, pp. 689-690).

## Separation Techniques

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1744 For dilute solutions of electrolytes ( $\leq 10^{-2}$  molar), the activity coefficient is approximately one  
1745 ( $\gamma \approx 1$ ; it approaches one as the solution becomes more dilute, becoming one under the ideal  
1746 conditions of infinite dilution). Then, the solubility product constant is expressed in terms of the  
1747 concentrations of ions in solution, the typical form in which the equation is found in most  
1748 chemistry textbooks:

1749 
$$K_{sp} = [M^{+n}]^m [N^{-m}]^n$$

1750 For strontium carbonate,  $K_{sp}$  is defined in terms of the concentrations of  $Sr^{+2}$  and  $CO_3^{-2}$ :

1751 
$$K_{sp} = [Sr^{+2}][CO_3^{-2}] = 1.6 \times 10^{-9}$$

1752 In order for the carbonate to precipitate, the product of the concentration of the ions in solution  
1753 representing the ions in the equilibrium expression, the *common ions*, must exceed the value of  
1754 the  $K_{sp}$ . The concentration of each common ion does not have to be equal. For example, if  $[Sr^{+2}]$   
1755 is  $1 \times 10^{-6}$  molar, then the carbonate ion concentration must be greater than 0.0016 molar for  
1756 precipitation to occur because  $(1 \times 10^{-6}) \times (.0016) = 1.6 \times 10^{-9}$ .

1757 At higher concentrations ( $\geq 10^{-2}$  molar), where the ions in solution deviate from ideal behavior,  
1758 the value of the activity coefficient decreases, and the concentrations of the ions do not  
1759 approximate their activities. Under these conditions, the concentrations do not reflect the  
1760 behavior of the dissolution equilibrium, and the equation cannot be used for precipitation or  
1761 solubility calculations. More complex estimations of activity coefficients must be made and  
1762 applied to the general equation (Birkett et al., 1988, pp. 2.6-1 to 2.6-24). Generally, radiochemi-  
1763 cal separations use an excess of a precipitating agent. The exact solution concentrations do not  
1764 need to be known but they should be high to ensure complete reaction. Practical radiochemical  
1765 separations performed based on solubility (either  $K_{sp}$  or coprecipitation phenomenon) are best  
1766 described by M.L. Salutsky (1959, pp. 744-755).

1767 Analysts often need to know if a precipitate will form when two solutions are mixed. For  
1768 example:

1769 "If a chemist mixes 100 mL of 0.0050 M NaCl with 200 mL of 0.020 M  $Pb(NO_3)_2$ , will lead  
1770 chloride precipitate? The *ion product*,  $Q$ , must be calculated and compared to  $K_{sp}$  for the  
1771 process:



1773 After the two solutions are mixed,  $[\text{Pb}^{+2}] = 1.3 \times 10^{-2} \text{ M}$  ( $0.2 \text{ L} \times 2.0 \times 10^{-2} \text{ M}/0.3 \text{ L}$ ), and  $[\text{Cl}^-]$   
 1774  $] = 1.7 \times 10^{-3} \text{ M}$  ( $0.1 \text{ L} \times 5.0 \times 10^{-3} \text{ M}/0.3 \text{ L}$ ). The value for the ion product is calculated from  
 1775 the expression

$$1776 \quad Q = [\text{Pb}^{+2}][\text{Cl}^-]^2 \text{ or } [1.3 \times 10^{-2}][1.7 \times 10^{-3}]^2$$

$$1777 \quad Q = 3.8 \times 10^{-8}$$

1778 The numerical value for  $K_{\text{sp}}$  is  $1.6 \times 10^{-5}$ . Because the ion product  $Q$  is less than  $K_{\text{sp}}$ , no  
 1779 precipitate will form. Only when the ion product is greater than  $K_{\text{sp}}$  will a precipitate form.”

1780 Conditions in the solution phase can affect solubility. For example, the solubility of an ion is  
 1781 lower in an aqueous solution containing a common ion, one of the ions comprising the  
 1782 compound, than in pure water because a precipitate will form if the  $K_{\text{sp}}$  is exceeded. This  
 1783 phenomenon is known as the *common ion effect* and is consistent with LeChatelier’s Principle.  
 1784 For example, the presence of soluble sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in solution with strontium ions  
 1785 can cause the precipitation of strontium carbonate, because carbonate ions from the sodium salt  
 1786 contribute to their overall concentration in solution and tend to reverse the solubility equilibrium  
 1787 of the “insoluble” strontium carbonate:



1790 Alternatively, if a complexing agent or ligand is available that can react with the cation of a  
 1791 precipitate, the solubility of the compound can be markedly enhanced. An example from Section  
 1792 14.3.4.3, “Formation and Dissolution of Precipitates,” provides an illustration of this  
 1793 phenomenon. In the determination of  $^{90}\text{Sr}$ ,  $\text{Sr}^{+2}$  is separated from the bulk of the solution by direct  
 1794 precipitation of the sulfate ( $\text{SrSO}_4$ ). The precipitate is redissolved by forming a complex ion with  
 1795 EDTA,  $\text{Sr}(\text{EDTA})^{-2}$ , to separate it from lanthanides and actinides (DOE, 1994, Method RP520):



1798 Additionally, many metal ions are weakly acidic and hydrolyze in solution. Hydrolysis of the  
 1799 ferric ion ( $\text{Fe}^{+3}$ ) a classical example of this phenomenon:

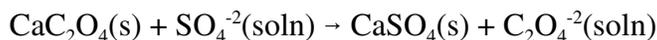
1800



1801 When these metal ions hydrolyze, producing a less soluble complex, the solubility of the salt is a  
1802 function of the pH of the solution, increasing as the pH decreases. The minimum solubility is  
1803 found under acidic conditions when the concentrations of the hydrolyzed species become  
1804 negligible. As demonstrated by Leussing, the solubility of a salt also depends upon the activity of  
1805 the solid phase. There are a number of factors that affect the activity of the solid phase (Leussing,  
1806 1959, pp. 690-692):

- 1807 • *Polymorphism* is the existence of a chemical substance in two or more crystalline forms. For  
1808 example, calcium carbonate can have several different forms; only one form of a crystal is  
1809 stable at a given temperature. At ordinary pressures and temperatures, calcite with a solubility  
1810 of 0.028 g/L, is the stable form. Aragonite, another common form of calcium carbonate  
1811 ( $\text{CaCO}_3$ ), has a solubility of 0.041g/L at these conditions. It is not necessarily calcite that  
1812 precipitates when solutions of sodium carbonate and calcium nitrate are mixed. Extremely  
1813 low concentrations of large cations, such as strontium, barium, or lead, promote the  
1814 precipitation of aragonite over calcite (Wray and Daniels, 1957). On aging, the more soluble  
1815 aragonite converts to calcite.
- 1816 • Various possible hydrates of a solid have different solubilities. For instance, at 25 °C, the  
1817 molar solubility of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is 0.206 and that of anhydrite ( $\text{CaSO}_4$ ) is 0.271.
- 1818 • The solid phase can undergo a reaction with a salt in solution.
- 1819 • Particle size of a solid can affect its solubility, because it has been demonstrated that the  
1820 solubility of smaller particles is greater than that of larger particles.
- 1821 • Age of a precipitate can affect solubility. For example, Biederman and Schindler (1957) have  
1822 demonstrated that the solubility of precipitated ferric hydroxide [ $\text{Fe}(\text{OH})_3$ ] undergoes a four-  
1823 fold decrease to a steady state after 200 hours.
- 1824 • Exchange of ions at the surface of the crystal with ions in the solution can affect the solubility  
1825 of a solid. This effect is a function of the amount of surface available for exchange and is,  
1826 therefore, greater for a finely divided solid. For example, Kolthoff and Sandell (1933)  
1827 observed that calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) can exchange with either sulfate or barium ions:

1828





1830 The excess of common ions that appears on the right-hand side of the equations represses  
1831 the solubility of calcium oxalate according to the laws of mass action.

1832 Ideally, separation of common ions from foreign ions in solution by precipitation will result in a  
1833 pure solid that is easy to filter. This method should ensure the production of a precipitate to meet  
1834 these criteria as closely as possible. The physical process of the formation of a precipitate is quite  
1835 complex, and involves both nucleation and crystal growth. *Nucleation* is the formation within a  
1836 supersaturated solution of the smallest particles of a precipitate (nuclei) capable of spontaneous  
1837 growth. The importance of nucleation is summarized by Salutsky (1959, p. 734):

1838 “The nucleation processes govern the nature and purity of the resulting precipitates. If the  
1839 precipitation is carried out in such a manner as to produce numerous nuclei, precipitation will  
1840 be rapid, individual crystals will be small, filtration and washing difficult, and purity low. On  
1841 the other hand, if precipitation is carried out so that only a few nuclei are formed, precipita-  
1842 tion will be slower, crystals larger, filtration easier, and purity higher. Hence, control of  
1843 nucleation processes is of considerable significance in analytical chemistry.”

1844 Once the crystal nuclei are formed, crystal growth proceeds through diffusion of the ions to the  
1845 surface of the growing crystal and deposition of those ions on the surface. This crystal growth  
1846 continues until supersaturation of the precipitating material is eliminated and equilibrium  
1847 solubility is attained.

1848 Thus, the goal is to produce fewer nuclei during precipitation so that the process will occur  
1849 slowly, within reasonable limits, and larger crystals will be formed. Impurities result from three  
1850 mechanisms: (1) inclusion, either by isomorphous replacement (isomorphic inclusion),  
1851 replacement of a common ion in the crystal structure by foreign ions of similar size and charge to  
1852 form a mixed crystal, or by solid solution formation (nonisomorphic inclusion), simultaneous  
1853 crystallization of two or more solids mixed together; (2) surface absorption of foreign ions; and  
1854 (3) occlusion, the subsequent entrapment of adsorbed ions as the crystal grows. Slow growth  
1855 gives the isomorphous ion time to be replaced by a common ion that fits the crystal structure  
1856 perfectly, producing a more stable crystal. It also promotes establishment of equilibrium  
1857 conditions for the formation of the crystal structure so that adsorbed impurities are more likely to  
1858 desorb and be replaced by a common ion rather than becoming entrapped. In addition, for a given  
1859 weight of the solid that is forming, a small number of large crystals present an overall smaller  
1860 surface area than a large number of small crystals. The large crystals provide less surface area for  
1861 impurities to adsorb.

1862 14.8.3.2 Factors Affecting Precipitation

1863 Several factors affect the nature and purity of the crystals formed during precipitation. A  
1864 knowledge of these factors permits the selection and application of laboratory procedures that  
1865 increase the effectiveness of precipitation as a technique for the separation and purification of  
1866 ions, and for the formation of precipitates that are easily isolated. These factors, summarized  
1867 from Berg (1963, pp. 251-284) and Salutsky (1959, pp. 736-742), include the following:

- 1868 • *Rate of precipitation.* Formation of large, well-shaped crystals is encouraged through slow  
1869 precipitation because fewer nuclei form and they have time to grow into larger crystals to the  
1870 detriment of smaller crystals present. Solubility of the larger crystals is less than that of  
1871 smaller crystals because smaller crystals expose more surface area to the solution. Larger  
1872 crystals also provide less surface area for the absorption of foreign ions. Slow precipitation  
1873 can be accomplished by adding a very dilute solution of the precipitant gradually, with  
1874 stirring, to a medium in which the resulting precipitate initially has a moderate solubility.
  
- 1875 • *Concentration of Ions and Solubility of Solids.* The rate of precipitation depends on the  
1876 concentration of ions in solution and the solubility of the solids formed during the  
1877 equilibrium process. A solution containing a low concentration of ions, but sufficient  
1878 concentration to form a precipitate, will slow the process, resulting in larger crystal  
1879 formation. At the same time, increasing the solubility of the solid, either by selecting the  
1880 counter-ion for precipitation or by altering the precipitating conditions, will also slow  
1881 precipitation. Many radionuclides form insoluble solids with a variety of ions, and the choice  
1882 of precipitating agent will affect the solubility of the precipitate. For example, radium sulfate  
1883 ( $\text{RaSO}_4$ ) is the most insoluble radium compound known. Radium carbonate ( $\text{RaCO}_3$ ) is also  
1884 insoluble, but its  $K_{sp}$  is greater than that of radium sulfate (Kirby and Salutsky, 1964, p. 9).
  
- 1885 • *Temperature.* Precipitation at higher temperature slows nucleation and crystal growth  
1886 because of the increased thermal motion of the particles in solution. Therefore, larger crystals  
1887 form, reducing the amount of adsorption and occlusion. However, most solids are more  
1888 soluble at elevated temperatures, effectively reducing precipitate yield; an optimum  
1889 temperature balances these opposing factors.
  
- 1890 • *Digestion.* Extremely small particles, with a radius on the order of one micron, are more  
1891 soluble than larger particles because of their larger surface area compared to their volume  
1892 (weight). Therefore, when a precipitate is heated over time (*digestion*) the small crystals  
1893 dissolve and larger crystals grow (*Ostwald ripening*). Effectively, the small crystals are  
1894 recrystallized, allowing the escape of impurities (occluded ions) and growth of larger crystals.

1895 This process reduces the surface area for adsorption of foreign ions and, at the same time,  
 1896 replaces the impurities with common ions that properly “fit” the crystal lattice. Recrystal-  
 1897 lization perfects the crystal lattice, producing a purer precipitate (see *Reprecipitation* below).  
 1898 Digestion is used in an  $^{131}\text{I}$  determination to increase the purity of the lead iodide ( $\text{PbI}_2$ )  
 1899 crystals (EPA, 1984, pp. I-01-1-9).

1900 • *Degree of Supersaturation.* A relatively high degree of supersaturation is required for  
 1901 spontaneous nucleation, and degree of supersaturation is the main factor in determining the  
 1902 physical character of a precipitate. Generally, the higher the supersaturation required, the  
 1903 more likely a curdy, flocculated colloid will precipitate because more nuclei form under  
 1904 conditions of higher supersaturation and crystal growth is faster. In contrast, the lower the  
 1905 supersaturation required, the more likely a crystalline precipitate will form because fewer  
 1906 nuclei form under these conditions and crystal growth is slower. Most perfect crystals are  
 1907 formed, therefore, from supersaturated solutions that require lower ion concentrations to  
 1908 reach the necessary degree of supersaturation and, as a result, inhibit the rate of nucleation  
 1909 and crystal growth. Degree of supersaturation ultimately depends on physical properties of  
 1910 the solid that affect its formation. Choice of counter-ion will determine the type of solid  
 1911 formed from a radionuclide, which, in turn, determines the degree of saturation required for  
 1912 precipitation. Many radionuclides form insoluble solids with a variety of ions, and the choice  
 1913 of precipitating agent will affect the nature of the precipitate.

1914 • *Solvent.* The nature of the solvent affects the solubility of an ionic solid (precipitate) in the  
 1915 solvent. The polarity of water can be reduced by the addition of other miscible solvents such  
 1916 as alcohols, thereby reducing the solubility of precipitates. Strontium chromate ( $\text{SrCrO}_4$ ) is  
 1917 soluble in water, but it is insoluble in a methyl alcohol ( $\text{CH}_3\text{OH}$ )-water mixture and can be  
 1918 effectively precipitated from the solution (Berg, 1963, p. 364). In some procedures,  
 1919 precipitation is achieved by adding alcohol to an aqueous solution, but the dilution effect  
 1920 might reduce the yield because it lowers the concentration of ions in solution.

1921 • *Ion Concentration.* The common-ion effect causes precipitation to occur when the  
 1922 concentration of ions exceeds the solubility-product constant. In some cases, however, excess  
 1923 presence of common ions increases the solubility of the precipitate by decreasing the activity  
 1924 of the ions in solution, as they become more concentrated in solution and deviate from ideal  
 1925 behavior. An increase in concentration of the ions is necessary to reach the activity of ions  
 1926 necessary for precipitate formation.

1927 • *Stirring.* Stirring the solution during precipitation increases the motion of particles in solution  
 1928 and decreases the localized buildup of concentration of ions by keeping the solution

1929 thoroughly mixed. Both of these properties slow nucleation and crystal growth, thus  
1930 promoting larger and purer crystals. This approach also promotes recrystallization because  
1931 the smaller crystals, with their net larger surface area, are more soluble under these  
1932 conditions. Virtually all radiochemical laboratories employ stirring with a magnetic stirrer  
1933 during precipitation reactions.

1934 • *Complex-Ion Formation.* Formation of complex ions can be used to *hold back* impurities  
1935 from precipitating by producing a more soluble form of a solid. The classical example of this  
1936 phenomenon is the precipitation of lead ( $\text{Pb}^{+2}$ ) in the presence of silver ions ( $\text{Ag}^{+1}$ ). Chloride  
1937 ion ( $\text{Cl}^{-1}$ ) is the precipitating agent that produces insoluble lead chloride ( $\text{PbCl}_2$ ). In an excess  
1938 of the agent, silver chloride ( $\text{AgCl}$ ) is not formed because a soluble salt containing the  
1939 complex ion,  $\text{AgCl}_2^{-1}$  is formed. Complex-ion formation is also used to form precipitates (see  
1940 Section 14.3, “Complexation”).

1941 • *pH Effect.* Altering the pH of aqueous solutions will alter the concentration of ions in the  
1942 precipitation equilibrium by the common-ion effect, if the hydrogen ion ( $\text{H}^{+1}$ ) or hydroxide  
1943 ion ( $\text{OH}^{-1}$ ) is common to the equilibrium. For example, calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) can be  
1944 precipitated or dissolved, depending on the pH of the solution, as follows:



1946 Because the oxalate concentration is affected by the hydrogen-ion concentration,



1948 increasing the hydrogen-ion concentration (lowering the pH) decreases the oxalate ion  
1949 concentration by forming bioxalate, which makes the precipitate more soluble. Therefore,  
1950 decreasing the hydrogen-ion concentration (raising the pH), therefore, aids precipitation.  
1951 Similar effects are obtained with carbonate precipitates:



1954 Many metal sulfides are formed in a solution of hydrogen sulfide by generating the sulfide  
1955 ion ( $\text{S}^{-2}$ ) at suitable pH:





1959 The pH can also influence selective formation of precipitates. Barium chromate will  
 1960 precipitate in the presence of strontium at pH 4 to 8, leaving strontium in solution. Sodium  
 1961 carbonate is added and strontium precipitates after ammonia (NH<sub>3</sub>) is added to make the  
 1962 solution more alkaline. This procedure is the basis for the separation of radium from  
 1963 strontium in the radioanalysis of strontium in drinking water (EPA, 1980, p. 63).

1964 • *Precipitation from Homogeneous Solution.* Addition of a precipitating agent to a solution of  
 1965 ions causes a localized excess of the reagent (higher concentrations) to form in the mixture.  
 1966 The excess reagent is conducive to rapid formation of a large number of small crystals,  
 1967 producing a precipitate of imperfect crystals that contains excessive impurities. The  
 1968 precipitate formed under these conditions is sometimes voluminous and difficult to filter.  
 1969 Localized excesses can also cause precipitation of more soluble solids than the expected  
 1970 precipitate.

1971 These problems largely can be avoided if the solution is homogenous in all stages of  
 1972 precipitate formation, and if the concentration of precipitating agent is increased, as slowly as  
 1973 practical, to cause precipitation from the most dilute solution possible. This increase in  
 1974 concentration is accomplished, not by adding the precipitating agent directly to the solution,  
 1975 but rather by generating the agent throughout the solution, starting with a very small  
 1976 concentration and slowly increasing the concentration while stirring. The precipitating agent  
 1977 is generated indirectly as the result of a chemical change of a reagent that produces the  
 1978 precipitating agent internally and homogeneously throughout the solution. The degree of  
 1979 supersaturation is low because the concentration of precipitating agent in solution is always  
 1980 uniformly low enough for nucleation only. This method produces larger crystals with fewer  
 1981 impurities.

1982 Table 14.11 (Salutsky, 1959, p. 741) summarizes methods used for precipitate formation  
 1983 from homogeneous solution. Descriptions of these methods can be found in Gordon et al.  
 1984 (1959).

1985 Some agents are generated by decomposition of a compound in solution. Hydrogen sulfide,  
 1986 for example, is produced from thioacetamide:



1988 Copper sulfide (CuS) coprecipitates technetium from a homogeneous medium by the  
 1989 generation of hydrogen sulfide by this method (EPA, 1973, pp. 67-72). Other agents alter the  
 1990 pH of the solution (see “pH Effect” above). Hydrolysis of urea, for example, produces  
 1991 ammonia, which raises the pH of a solution:



1993 **TABLE 14.11 — Summary of methods for utilizing precipitation**  
 1994 **from homogeneous solution<sup>(1)</sup>**

Precipitant	Reagent	Element Precipitated
Hydroxide	Urea	Al, Ga, Th, Fe(III), Sn, and Zr
	Acetamide	Ti
	Hexamethylenetetraamine	Th
	Metal Chelate and H <sub>2</sub> O <sub>2</sub>	Fe(III)
Phosphate	Triethyl Phosphate	Zr and Hf
	Trimethyl Phosphate	Zr
	Metaphosphoric Acid	Zr
	Urea	Mg
Oxalate	Dimethyl Oxalate	Th, Ca, Am, Ac, and Rare Earths
	Diethyl Oxalate	Mg, Zn, and Ca
	Urea and an Oxalate	Ca
Sulfate	Dimethyl Sulfate	Ba, Ca, Sr, and Pb
	Sulfamic Acid	Ba, Pb, and Ra
	Potassium Methyl Sulfate	Ba, Pb, and Ra
	Ammonium Persulfate	Ba
	Metal Chelate and Persulfate	Ba
Sulfide	Thiocetamide	Pb, Sb, Bi, Mo, Cu, and As, Cd, Sn, Hg, and Mn
Iodate	Iodine and Chlorate	Th and Zr
	Periodate and Ethylene Diacetate (or β-Hydroxy Acetate)	Th and Fe(III)
	Ce(III) and Bromate	Ce(IV)
Carbonate	Trichloroacetate	Rare Earths, Ba, and Ra
Chromate	Urea and Dichromate	Ba and Ra
	Potassium Cyanate and Dichromate	Ba, Ra
	Cr(III) and Bromate	Pb
Periodate	Acetamide	Pb
Chloride	Silver Ammonia Complex and β-Hydroxyethyl Acetate	Ag
Arsenate	Arsenite and Nitrite	Zr

Precipitant	Reagent	Element Precipitated
Tetrachlorophthalate	Tetrachlorophthalic Acid	Th
Dimethylgloxime	Urea and Metal Chelate	Ni
8-Hydroxyquinoline	Urea and Metal Chelate	Al
Fluoride	Fluoroboric Acid	La

(1) Salutsky, 1959, p. 741

- *Reprecipitation.* This approach increases the purity of precipitates. During the initial precipitation, crystals collected contain only a small amount of foreign ions relative to the common ions of the crystal. When the precipitate is redissolved in pure solvent, the foreign ions are released into solution, producing a concentration of impurities much lower than that in the original precipitating solution. On reprecipitation, a small fraction of impurities is carried down with the precipitate, but the relative amount is much less than the original because their concentration in solution is less. Nevertheless, foreign ions are not eliminated because absorption is greater at lower, rather than at higher, concentrations. On balance, reprecipitation increases the purity of the crystals. Reprecipitation is used in the procedure to determine americium (Am) in soil (DOE, 1990 and 1997, Method Am-01). After americium is coprecipitated with calcium oxalate ( $\text{CaC}_2\text{O}_4$ ), the precipitate is reprecipitated to purify the solid.

#### 14.8.3.3 Optimum Precipitation Conditions

There is no single, fixed rule to eliminate all impurities during precipitation (as discussed in the section above), but over the years, a number of conditions have been identified from practical experience and theoretical considerations that limit these impurities (Table 14.12). Precipitations are generally carried out from dilute solutions adding the precipitant slowly with some form of agitation to a hot solution. Normally, the precipitant is then allowed to age before it is removed by filtration and washed. Reprecipitation is then commonly performed. Reprecipitation is one of the most powerful techniques available to the analyst because it increases purity, regardless of the form of the impurity.

Table 14.12 highlights the optimum precipitation conditions to eliminate impurities.

2034

**TABLE 14.12 — Influence of precipitation conditions on the purity of precipitates** <sup>(1,2)</sup>

2035

Condition	Form of Impurity			
	Mixed Crystals	Surface Adsorption	Occlusion and Inclusion	Post-precipitation
Dilute solutions	○	+	+	○
Slow precipitation	+	+	+	-
Prolonged digestion	-	+	+	-
High temperature	-	+	+	-
Agitation	+	+	+	○
Washing the precipitate	○	+	○	○
Reprecipitation	+	+	+	○

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(1) +, increased purity; -, decreased purity; ○, little or no change in purity

(2) Salutsky, 1959, p. 764

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#### 14.8.4 Coprecipitation

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In many solutions, especially those of environmental samples, the concentration of the radionuclide of interest is too low to cause precipitation, even in the presence of high concentrations of its counter-ion, because the product of the concentrations does not exceed the solubility product. Radium in most environmental samples, for example, is not present in sufficient concentration to cause its very insoluble sulfate ( $\text{RaSO}_4$ ) to precipitate. The radionuclide can often be brought down selectively and quantitatively from solution during precipitation of an alternate insoluble compound by a process called *coprecipitation*. The insoluble compound commonly used to coprecipitate radium isotopes in many radioanalytical procedures is another insoluble sulfate, barium sulfate ( $\text{BaSO}_4$ ) (EPA, 1984, Method Ra-01; EPA, 1980, Method 900.1). The salt is formed with barium, also a member of the alkaline earth family of elements with chemical properties very similar to those of radium. Alternatively, a different salt that is soluble for the radionuclide can be used to cause coprecipitation. Radium can be coprecipitated with lanthanum fluoride, even though radium fluoride is soluble itself. For trace amounts of some radionuclides, other isotopic forms of the element are available that can be added to the solution to bring the total concentration of all forms of the element to the level that will result in precipitation. For trace quantities of  $^{90}\text{Sr}$ , inactive strontium ( $^{85}\text{Sr}$ ), which will not interfere with the radioanalysis of  $^{90}\text{Sr}$ , is added to permit the precipitation of strontium carbonate in the presence of carbonate ions. The added ion that is present in sufficient concentration to cause a precipitate to form is called a carrier (Section 14.9, “Carriers and Tracers”). Barium, lanthanum, and stable strontium, respectively, are carriers in these examples (DOE, 1995, Method RP5001; DOE, 1990 and 1997, Method Sr-02; EPA, 1984, Sr-04). The

2067 term carrier is also used to designate the insoluble compound that causes coprecipitation. Barium  
2068 sulfate, lanthanum fluoride ( $\text{LaF}_3$ ), and strontium carbonate are sometimes referred to as the  
2069 carrier in these coprecipitation procedures. See Wahl and Bonner (1951, p. 403) for additional  
2070 examples of tracers and their carriers used for coprecipitation.

2071 The common definition of coprecipitation is, “the contamination of a precipitate by substances  
2072 that are normally soluble under the conditions of precipitation” (Salutsky, 1959, p. 748). In a very  
2073 broad sense, coprecipitation is alternately defined as the precipitation of one compound  
2074 simultaneously with one or more other compounds to form mixed crystals (Berg, 1963, p. 296).  
2075 Each is present in macro concentrations (i.e., sufficient concentrations to exceed the solubility  
2076 product of each). As the term is used in radiochemistry, coprecipitation is the simultaneous  
2077 precipitation of one compound that is normally soluble under the conditions of precipitation with  
2078 one or more other compounds that form a precipitate under the same conditions. Coprecipitation  
2079 of two or more rare earths as oxalates, barium and radium as sulfates, or zirconium (Zr) and  
2080 hafnium (Hf) as phosphates are examples of this broader definition (Salutsky, 1959, p. 748). By  
2081 either definition, coprecipitation introduces foreign ions into a precipitate as impurities that  
2082 would normally be expected to remain in solution; and precipitation techniques, described in the  
2083 previous section, are normally used to maximize this effect while minimizing the introduction of  
2084 true impurities. As a method to separate and collect radionuclides present in solution at very low  
2085 concentration, coprecipitation is performed in a controlled process to associate the ion of choice  
2086 selectively with a precipitate, while excluding other foreign ions that would interfere with the  
2087 analytical procedure.

#### 2088 14.8.4.1 Coprecipitation Processes

2089 In order to choose the best conditions to coprecipitate an ion selectively, two processes should be  
2090 considered. First is precipitation itself and the appropriate techniques employed to minimize  
2091 association of impurities (see Section 14.8.3). Second is coprecipitation mechanisms and the  
2092 controlling factors associated with each. Three processes (described above in Section 14.8.3.1,  
2093 “Solubility and the Solubility Product Constant”) are responsible for coprecipitation, although  
2094 the distinction between these processes is not always clear (Hermann and Suttle, 1961, p. 1369).  
2095 They consist of: (1) inclusion, i.e., uptake from solution of an ion similar in size and charge to  
2096 the solid forming the precipitate in order to form a mixed crystal or solid solution; (2) surface  
2097 adsorption; and (3) occlusion (mechanical entrapment).

2098 *Inclusion.* If coprecipitation is accomplished from a homogeneous solution allowing the crystals  
2099 to form slowly in an orderly manner, then inclusion contributes to the coprecipitation process.

2100 Under these conditions, the *logarithmic distribution law* applies, which represents the most  
2101 efficient coprecipitation method that involves mixed crystals (Salutsky, 1959, p. 750):

2102 
$$\log(I_i/I_f) = \lambda \log(P_i/P_f)$$

2103 In the equation,  $I_i$  is the concentration of impurity in solution at the start of crystallization and  $I_f$   
2104 is the concentration at the end.  $P$  represents the corresponding concentration of the primary ion in  
2105 solution.  $\lambda$ , is the *logarithmic distribution coefficient* and is a constant. Values of  $\lambda$  for  
2106 some tracers distributed in solid carriers can be found in Wahl and Bonner (1951, p. 393).  
2107  $\lambda$  values greater than one represent removal of a foreign ion by inclusion during  
2108 coprecipitation. The larger the value of  $\lambda$ , the more effective and selective for a specific ion  
2109 the process is.  $\lambda$  is also inversely proportional to the rate of precipitation. Slow  
2110 precipitation, as accomplished by homogeneous precipitation, results in larger values and more  
2111 efficient coprecipitation. For example, “Actinium [Ac] has been selectively removed from  
2112 solutions containing iron and aluminum [Al] through slow oxalate precipitation by the controlled  
2113 hydrolysis of dimethyl oxalate” (Hermann and Suttle, 1961, p. 1376). Also, as described in  
2114 Section 14.8.3.2, “Factors Affecting Precipitation,” technetium is coprecipitated with copper  
2115 sulfide (CuS) carrier produced by the slow generation of hydrogen sulfide ( $H_2S$ ) as thioacetamide  
2116 is hydrolyzed in water (EPA, 1973, pp. 67-72).

2117 Generally,  $\lambda$  decreases as the temperature increases; thus, coprecipitation by inclusion is favored  
2118 by lower temperature.

2119 Digestion of the precipitate at elevated temperature over lengthy time periods—a process that  
2120 promotes recrystallization and purer crystals—will often cause mixed crystals to form by an  
2121 alternate mechanism (i.e., *homogeneous distribution*) that is not as efficient, but which is often as  
2122 successful as logarithmic distribution. The *equilibrium distribution law* is represented by  
2123 (Salutsky, 1959, p. 749):

2124 
$$(I/P)_{ppt.} = D (I/P)_{soln.}$$

2125 where  $I$  represents the amount of impurity and  $P$  the amount of primary substance forming the  
2126 precipitate. The symbol  $D$  is the *homogeneous distribution coefficient*. Values of  $D$  greater than  
2127 one represent removal of a foreign ion by inclusion during coprecipitation. Some values of  $D$  can  
2128 be found in Wahl and Bonner (1951, p. 393). According to Hermann and Suttle:

2129 “Homogeneous distribution is conveniently obtained at ordinary temperatures by rapid  
2130 crystallization from supersaturated solutions with vigorous stirring. Under such conditions

2131 the precipitate first formed is very finely divided, the recrystallization of the minute crystals  
2132 is rapid, and each molecule (sic) passes many times between solution and precipitate. If this  
2133 process is repeated often enough, an equilibrium between solid and solution is obtained, and  
2134 all the resulting crystals grow from a solution of constant composition” (Hermann and Suttle,  
2135 1961, pp. 1473-1474).

2136 In either case, optimal results are obtained through inclusion when the precipitate contains an ion  
2137 with chemical properties similar to those of the foreign ion, although it is not necessary for the  
2138 similarity to exist in every successful coprecipitation. Barium sulfate is very successful in  
2139 coprecipitating  $Ra^{+2}$ , primarily because radium is in the same chemical family as barium, and has  
2140 the same charge and a similar ionic radius. For best results, the radius of the foreign ion should  
2141 be within approximately 15 percent of that of one of the common ions in the precipitate  
2142 (Hermann and Suttle, 1961, p. 1479).

2143 *Surface Adsorption.* During surface adsorption, ions are adsorbed from solution onto the surfaces  
2144 of precipitated particles. The conditions leading to surface adsorption are described by Salutsky:

2145 “The surface of a precipitate is particularly active. Ions at the surface of a crystal (unlike  
2146 those within the crystal) are incompletely coordinated and, hence are free to attract other ions  
2147 of opposite charge from solution” (Salutsky, 1959, p. 754).

2148 Adsorption involves a primary adsorption layer that is held very tightly, and a counter-ion layer  
2149 held more loosely. Ions common to the precipitate are adsorbed most strongly at the surface to  
2150 continue growth of the crystal. During precipitation of  $BaSO_4$ , barium ions ( $Ba^{+2}$ ) and sulfate ions  
2151 ( $SO_4^{-2}$ ) are the primary ions adsorbed. If only one of the common ions remains in solution, then  
2152 foreign ions of the opposite charge are adsorbed to maintain electrical neutrality. When barium  
2153 sulfate is precipitated from a solution containing excess barium ions, for example, foreign ions  
2154 such as  $Cl^{-1}$ , if present, are adsorbed after sulfate ions are depleted in the precipitation process.  
2155 Foreign ions of the same charge, such as  $Na^{+1}$ , are repelled from the surface. Surface adsorption  
2156 can be controlled, therefore, by controlling the concentration of ions during precipitation or by  
2157 the addition of ions to alter the concentration. A precipitate of silver chloride ( $AgCl$ ) in excess  
2158  $Ag^{+1}$  repels  $^{212}Pb^{+2}$ , but in a solution containing an equal quantity of the common silver and  
2159 chloride ions, approximately 2 percent of  $^{212}Pb$  is adsorbed (Salutsky, 1959, pp. 754-755). In  
2160 contrast, almost 86 percent of  $^{212}Pb$  is adsorbed if an iodide solution is added to precipitate the  
2161 silver ions as silver iodide ( $AgI$ ), thereby reducing the concentration of silver ions and making  
2162 the chloride ion in excess in the solution. According to the *Paneth-Fajans-Hahn adsorption rule*,  
2163 the ion most adsorbed will be the one that forms the least soluble compound with an ion of the  
2164 precipitate. For example, barium sulfate in contact with a solution containing excess sulfate ions

2165 will adsorb ions of  $Pb > Ca > K > Na$ , which reflects the order of solubility of the respective  
2166 sulfates: thus,  $PbSO_4 < CaSO_4 < K_2SO_4 < Na_2SO_4$  (Salutsky, 1959, p. 755).

2167 “Because adsorption is a surface phenomenon, the larger the surface area of a precipitate, the  
2168 greater the adsorption of impurities” (Salutsky, 1959, p. 755). For that reason, colloidal crystals  
2169 exhibit a high degree of nonspecific adsorption. When a colloid is flocculated by the addition of  
2170 an electrolyte, the electrolyte can be adsorbed as an impurity. This interference largely can be  
2171 eliminated by aging the precipitate, thereby growing larger crystals and reducing the surface area.  
2172 Additionally, nonvolatile impurities can be replaced on the particle by washing the colloidal  
2173 precipitate with a dilute acid or ammonium salt solution. Well-formed large crystals exhibit  
2174 much less adsorption, and adsorption is not a significant factor in coprecipitation with these  
2175 solids. The tendency for a particular ion to be adsorbed depends on, among other factors, charge  
2176 and ionic size (Berg, 1963, p. 299). Large ions with a high charge exhibit high adsorption  
2177 characteristics: a high ionic charge increases the electrostatic attraction to the charged surface,  
2178 and an ion with a large radius is less hydrated by the solution and not as attracted to the solution  
2179 phase.

2180 “The amount of adsorption is also affected by prolonged standing of the precipitate in contact  
2181 with the solution. The fraction adsorbed is higher for some tracer ions, while the fraction is lower  
2182 for others. Recrystallization occurring during standing decreases the surface area so that the  
2183 fraction of tracer carried will decrease unless the tracer is trapped in the growing crystals ... in  
2184 which case the fraction carried may increase.” (Wahl, 1951, p. 117).

2185 Adsorption also depends on the concentration of an ion in solution (Berg, 1963, p. 299). A high  
2186 concentration of impurity increases the probability of solute interaction at the solid surface and  
2187 favors adsorption. Salutsky comments on the percent adsorption:

2188 “Generally, the percent adsorption is much greater at low concentrations than at high  
2189 concentrations. At very high concentrations of impurity, adsorption reaches a maximum  
2190 value, i.e., the adsorption is saturated” (Salutsky, 1959, pp. 755-756).

2191 *Occlusion.* Occlusion of an impurity within a precipitate results when the impurity is trapped  
2192 mechanically by subsequent crystal layers. For that reason, occluded impurities cannot be  
2193 physically removed by washing. Occlusion is more prevalent with colloidal precipitates than with  
2194 large crystals because of the greater surface area of colloidal solids. Freshly prepared hydroxides  
2195 and sulfides commonly contain occluded impurities, but most of them are released upon aging of  
2196 the precipitate.

2197 Mechanical entrapment occurs particularly when the precipitating agent is added directly to a  
2198 solution. Because of the localized high concentrations of precipitant, impurities are precipitated  
2199 that become occluded by the subsequent precipitation of the primary substance. The speed of the  
2200 precipitation process also affects the extent of occlusion. Occlusion can be reduced, therefore, by  
2201 homogeneous precipitation. Coprecipitation of strontium by barium sulfate, for example, is  
2202 accomplished by the homogeneous generation of sulfate by the hydrolysis of dimethylsulfate,  
2203  $(\text{CH}_3)_2\text{SO}_4$  (Hermann and Suttle, 1961, p. 1480). Digestion also eliminates occluded particles as  
2204 the solid is recrystallized. Considerable occlusion occurs during nucleation, and, therefore,  
2205 reducing the precipitation rate by lowering the temperature and reducing the number of nuclei  
2206 formed reduces the initial coprecipitation by occlusion.

2207 This type of coprecipitation is not limited to solid impurities. Sometimes the solvent and other  
2208 impurities dissolved in the solvent become trapped between layers of crystals. This *liquid*  
2209 *occlusion* is common in numbers of minerals such as quartz and gypsum.

#### 2210 14.8.4.2 Water as an Impurity

2211 In addition to other impurities, all precipitates formed from aqueous solutions contain water  
2212 (Salutsky, 1959, pp. 761-763). This water might be *essential water*, present as an essential part of  
2213 the chemical composition (e.g.,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), or it might be *nonessential*  
2214 *water*. Nonessential water can be present in the precipitate as hygroscopic water, surface water,  
2215 or included water. *Hygroscopic water* refers to the water that a solid adsorbs from the surround-  
2216 ing atmosphere. Many colloidal precipitates are highly hygroscopic because of their large  
2217 surface areas. Moreover, water can be adsorbed to the surface of the precipitate or included  
2218 within the crystal matrix, as described previously.

#### 2219 14.8.4.3 Postprecipitation

2220 Postprecipitation results when a solution contains two ions, one that is rapidly precipitated and  
2221 another that is slowly precipitated by the precipitating agent (Kolthoff et al., 1969, p. 245). The  
2222 first precipitate is usually contaminated by the second one. For example, calcium oxalate is a  
2223 moderately insoluble compound that can be precipitated quantitatively with time. Because the  
2224 precipitation tends to be slow, the precipitate is allowed to remain in contact with the solution for  
2225 some time before filtering. Magnesium oxalate is too soluble to precipitate on its own under  
2226 normal conditions. As long as the solution contains a predominance of calcium ions, very little  
2227 magnesium precipitates. However, as the precipitation of calcium approaches quantitative levels,  
2228 the competition of calcium and magnesium ions for adsorption at the surface becomes more  
2229 intense. As time progresses, the magnesium oxalate adsorbed on the surface acts as seed to

2230 induce the post-precipitation of a second solid phase of magnesium oxalate ( $\text{MgC}_2\text{O}_4$ ). Once  
2231 precipitated, the magnesium oxalate is only slightly soluble and does not redissolve.

2232 14.8.4.4 Coprecipitation Methods

2233 Selective coprecipitation of a radionuclide with an insoluble compound is primarily  
2234 accomplished by the judicious selection of the compound that forms the precipitate and the  
2235 concentration of solutions used in the precipitate's formation. Using good precipitation technique  
2236 minimizes the coprecipitation of impurities. The compound, then, should maximize  
2237 coprecipitation of the select radionuclide while providing a well-formed solid that attracts a  
2238 minimum of other foreign ions as impurities. In general, conditions that favor precipitation of a  
2239 substance in macroamounts also favor the coprecipitation of the same material from tracer  
2240 concentrations (i.e., too low for precipitate formation) with a foreign substance (Friedlander  
2241 et al., 1981, p. 294). Wahl and Bonner provide a useful summary for coprecipitation of a tracer  
2242 by a carrier:

2243 "In general a tracer is efficiently carried by an ionic precipitate if: (1) the tracer ion is  
2244 isomorphously incorporated into the precipitate, or (2) the tracer ion forms a slightly soluble  
2245 or slightly dissociated compound with the oppositely charged lattice ion and if the precipitate  
2246 has a large surface with charge opposite to that of the tracer ion (i.e., presence of excess of  
2247 the oppositely charged lattice ion)" (Wahl and Bonner, 1951, p. 105).

2248 Considering the principles of precipitation and coprecipitation, radium is coprecipitated  
2249 quantitatively with barium sulfate using excess sulfate in solution because: (1) radium forms the  
2250 least soluble sulfate of the other elements in the alkaline earth family (Paneth-Fajans-Hahn  
2251 adsorption rule); (2) the radium ion carries the same charge as the barium ion and is very similar  
2252 in size (inclusion); and 3) an excess of sulfate preferentially creates a common-ion layer on the  
2253 crystalline solid of sulfate ions that attracts barium ions and similar ions such as radium  
2254 (absorption). For example, in a procedure to determine  $^{226}\text{Ra}$  in water samples, radium is  
2255 coprecipitated as barium sulfate using 0.36 moles of sulfate with 0.0043 moles of barium, a large  
2256 excess of sulfate (EPA, 1984, Method Ra-03).

2257 The isolation of microquantities of tracers often occurs in two steps: first the tracer is separated  
2258 by coprecipitation with a carrier, and then it is separated from the carrier (Hermann and Suttle,  
2259 1961, p. 1486). Use of carriers that can be easily separated from the tracer is helpful, therefore,  
2260 coprecipitation by inclusion is not generally used. Coprecipitation by surface adsorption on  
2261 unspecific carriers is the most common method employed. Manganese dioxide  $\text{MnO}_2$ , sulfides  
2262 ( $\text{MnS}$ ), and hydroxides  $[\text{Mn}(\text{OH})_2]$  are important nonspecific carries because of their high surface

2263 areas. Ferric hydroxide [Fe(OH)<sub>3</sub>] is very useful for adsorbing cations, because it forms a very  
 2264 finely divided precipitate with a negative charge in excess hydroxide ion. Ferric hydroxide is  
 2265 used, for example, to collect plutonium in solution after it has been isolated from tissue (DOE,  
 2266 1990 and 1997, Method Pu-04). Tracers can be separated by dissolving the solid in acid and  
 2267 extracting the iron in ether.

2268 “The amount of ion adsorbed depends on its ability to compete with other ions in solution.  
 2269 Ions capable of displacing the ions of the radioelements are referred to as holdback carriers  
 2270 (see Section 14.9.2.4, *Holdback Carriers*). Highly charged ions, chemical homologs, and ions  
 2271 isotopic with the radioelement are among the most efficient displacers. Thus, the addition of  
 2272 a little inactive strontium makes it possible to precipitate radiochemically pure radiobarium  
 2273 as the nitrate or chloride in the presence of radiostrontium” (Hermann and Suttle, 1961, p.  
 2274 1487)

2275 Tables 14.13 and 14.14 provide more details about common coprecipitating agents for  
 2276 radionuclides.

**TABLE 14.13 — Common coprecipitating agents for radionuclides<sup>(1)</sup>**

Radionuclide	Oxidation State	Coprecipitate	Carrier <sup>(2)</sup>	Notes
Am	13	hydroxide iodate fluoride, oxalate, phosphate, hydroxide oxalate acetate fluoride, sulfate acetate	Am <sup>+3</sup> , Fe <sup>+3</sup> Ce <sup>+4</sup> , Th <sup>+4</sup> , Zr <sup>+4</sup> La <sup>+3</sup> , Ce <sup>+3</sup> , Nd <sup>+3</sup> , Bi <sup>+3</sup>  Ca <sup>+2</sup> Am <sup>+4</sup> La <sup>+3</sup> UO <sub>2</sub> <sup>+2</sup>	
Cs	+1	phosphomolybdate, chloroplatinate, bismuthnitrate, silicomolybdate	Cs <sup>+1</sup>	
Co	+2	hydroxide potassiumcobaltnitrate 1-nitroso-2-naphthol sulfide	Co <sup>+2</sup> Co <sup>+2</sup> Co <sup>+2</sup> Co <sup>+2</sup>	
Fe	+3	hydroxide ammoniumpyrouranate	Fe <sup>+3</sup> Fe <sup>+3</sup>	
I	-1	iodide	Pb <sup>+2</sup> , Ag <sup>+1</sup> , Pd <sup>+2</sup>	
Ni	+2	dimethylglyoxime hydroxide	Ni <sup>+2</sup>	
Nb	+5	hydroxide, phosphate	Nb <sup>+5</sup>	

Separation Techniques

Radionuclide	Oxidation State	Coprecipitate	Carrier <sup>(2)</sup>	Notes
2286 Po	+4	tellurium tellurate selenium dioxide hydroxide sulfide	Te Pb <sup>+2</sup> Se or Se <sup>-2</sup> Mn <sup>+4</sup> Fe <sup>+3</sup> , Al <sup>+3</sup> , La <sup>+3</sup> Cu <sup>+2</sup> , Bi <sup>+2</sup> , Pb <sup>+2</sup>	tellurate reduced with SnCl <sub>2</sub>
2287 Pu	+3 +4 +6	fluoride sulfate fluoride oxalate, iodate phosphate sodium uranylacetate	La <sup>+3</sup> , Nd <sup>+3</sup> , Ce <sup>+3</sup> , Ca <sup>+2</sup> La <sup>+3</sup> (K <sup>+1</sup> ) La <sup>+3</sup> , Nd <sup>+3</sup> , Ce <sup>+3</sup> Th <sup>+4</sup> Zr <sup>+2</sup> , Bi <sup>+3</sup> UO <sub>2</sub> <sup>+2</sup>	
2288 Ra	+2	hydroxide sulfate, chromate, chloride, bromide oxalate, phosphate fluoride	Fe <sup>+3</sup> Ba <sup>+2</sup> Th <sup>+4</sup> , Ca <sup>+2</sup> , Ba <sup>+2</sup> La <sup>+3</sup>	
2289 Sr	+2	carbonate nitrate chromate sulfate phosphate hydroxide	Sr <sup>+2</sup> , Ba <sup>+2</sup> , Ca <sup>+2</sup> Sr <sup>+2</sup> , Ba <sup>+2</sup> Ba <sup>+2</sup> Sr <sup>+2</sup> , Ca <sup>+2</sup> , Pb <sup>+2</sup> Sr <sup>+2</sup> Fe <sup>+3</sup>	alkaline pH
2290 Tc	+4 +7	hydroxide chlorate, iodate, perruthenate, tetrafluoroborate sulfide	Tc <sup>+4</sup> , Fe <sup>+3</sup> , Mn <sup>+2</sup> (Phenyl) <sub>4</sub> As <sup>+1</sup> Tc <sup>+7</sup> , Re <sup>+7</sup> , Cu <sup>+2</sup> , Cd <sup>+2</sup>	
2291 Th	+4	hydroxide fluoride iodate phosphate, peroxide sulfate oxalate	Th <sup>+4</sup> , La <sup>+3</sup> , Fe <sup>+3</sup> , Zr <sup>+3</sup> , Ac <sup>+3</sup> , Zn <sup>+2</sup> Th <sup>+4</sup> , La <sup>+3</sup> , Nd <sup>+3</sup> , Ce <sup>+3</sup> Th <sup>+4</sup> , Zr <sup>+3</sup> Th <sup>+4</sup> , Bi <sup>+3</sup> Ba <sup>+2</sup> Ca <sup>+2</sup>	
2292 U	+4	cupferron, pyrophosphate, phosphate, iodate, sulfate, oxalate	U <sup>+4</sup>	
		fluoride	La <sup>+3</sup> , Nd <sup>+3</sup>	
	+5	phosphate	Zr <sup>+3</sup>	
		sulfate	Ca <sup>+2</sup>	
	+6	cupferron	U <sup>+6</sup>	neutral solution
		pyrouranate	U <sup>+6</sup>	from aqueous NH <sub>3</sub> , many ions stay in solution as NH <sub>3</sub> complex

Radionuclide	Oxidation State	Coprecipitate	Carrier <sup>(2)</sup>	Notes
		phosphate	U <sup>+6</sup> , Al <sup>+3</sup>	
		peroxide	U <sup>+6</sup>	Th <sup>+4</sup> , Zr <sup>+3</sup> also coprecipitate
		hydroxide	Fe <sup>+3</sup>	without carbonate
		fluoride	Th <sup>+4</sup>	
Zr <sup>+4</sup>				

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- (1) Compiled from: Anders, 1960; Booman and Rein, 1962; Cobble, 1964; EPA, 1973; 1980; 1984; DOE, 1990, 1995, 1997; Finston and Kinsley, 1961, Grimaldi, 1961; Grindler, 1962; Hyde, 1960; Kallmann, 1961; Kallmann, 1964; Kirby and Salutsky, 1964; Metz and Waterbury, 1962; Sedlet, 1964; Sundermann and Townley, 1960; and Turekian and Bolter, 1966.
- (2) If the radionuclide itself is listed, alternate isotopic forms are sometimes used as carriers to form the precipitate.

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**TABLE 14.14 — Coprecipitation behavior of plutonium and neptunium**

Carrier Compound	Pu(III)	Pu(IV)	Pu(VI)	Np(IV)	Np(V)	Np(VI)
Hydroxides	C	C	C	C	C	C
Calcium fluoride	C	C		C		
Lanthanum fluoride	C	C	NC	C	C	NC
Barium sulfate	C	C	NC	C	NC	NC
Phosphates:						
Calcium phosphate	C	C		C		
Bismuth phosphate	C	C		C	NC	NC
Zirconium phosphate	NC	C	NC	C	NC	NC
Thorium pyrophosphate	NC	C	NC			
Thorium hypophosphate		C	NC			
U(IV) hypophosphate		C	NC			
Oxalates:						
Lanthanum oxalate	C	C	NC	NC		
Bismuth oxalate	C	C	NC			
Thorium oxalate	C	C	NC	C		
U(IV) oxalate	C	C	NC			
Iodates:						
Zirconium iodate		C	NC	C		
Ceric iodate		C	NC	C		
Thorium iodate		C	NC	C		NC
Sodium uranyl acetate	NC	NC	C	NC	Poor	C
Zirconium phenylarsenate	NC	C	NC	C	Poor	NC
Thorium peroxide		C		C		
Bismuth arsenate		C	NC	C		

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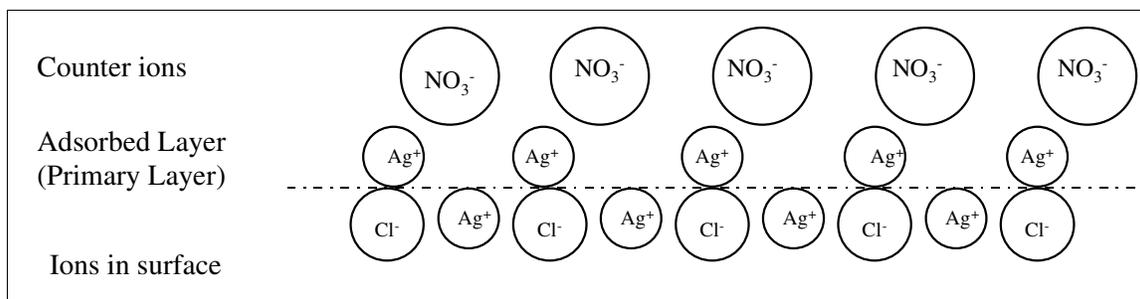
2327

“C” indicates nearly quantitative coprecipitation under proper conditions; “NC” indicates that coprecipitation can be made less than 1-2 percent under proper conditions. [Data compiled from Seaborg and Katz, Korkisch (1969), and the NAS-NS 3050, 3058 and 3060 monographs.]

2328 **14.8.5 Colloidal Precipitates**

2329 Many precipitates exhibit colloidal properties, especially when freshly formed (Salutsky, 1959,  
 2330 p. 744). The term “colloid state” refers to the dispersion of one phase that has colloidal  
 2331 dimensions (less than one micrometer, but greater than one nanometer) within a second phase. A  
 2332 *colloidal solution* is a colloid in which the second phase is a liquid (also known as a *sol*).  
 2333 However, in radiochemistry, a colloid refers to the dispersion of solid particles in the solution  
 2334 phase. The mixture is not a true solution: particles of the dispersed phase are larger than typical  
 2335 ions and molecules, and can often be viewed by a light microscope. Colloidal precipitates are  
 2336 usually avoided in analytical procedures because they are difficult to filter and to wash.  
 2337 Moreover, the purity of the precipitate is controlled by the tremendously large surface area of the  
 2338 precipitate and by the localized electrical character of the colloidal surface.

2339 The stability of colloidal solutions and suspensions is governed by two major forces, one of  
 2340 attraction between the particles (van der Waals) and one of repulsion (electrical double layer)  
 2341 (Salutsky, 1959, p. 745). This repulsive force is a result of the adsorptive capacity of the colloidal  
 2342 particles for their own ions. For instance, when silver chloride is precipitated in the presence of  
 2343 excess silver ions, the particles adsorb silver ions and become positively charged. Then counter-  
 2344 ions of opposite charge (in this case, nitrate ions) tend to adsorb to the particles to form a second  
 2345 electrical layer, as illustrated in Figure 14.5.



**FIGURE 14.5 — The electrical double layer: A schematic representation of adsorption of nitrate counter-ions onto a primary adsorbed layer of silver ions at the surface of a silver chloride crystal (Peters et al., 1974).**

2346 In a similar fashion, in the presence of a slight excess of alkali chloride, the silver chloride  
 2347 particles would adsorb chloride ions and become negatively charged. Therefore, precipitates  
 2348 brought down in the presence of an excess of one of the lattice ions tend to be contaminated with  
 2349 ions of the opposite charge. Moreover, because all of the particles have the same charge, they  
 2350 repel each other. If these repulsive forces exceed the attractive van der Waals’ forces, a stable  
 2351 colloid results, and the tightness with which the counter-ions are held in and with the water layer,

2352 or the completeness with which they cover the primary adsorbed ion layer, determines the  
2353 stability of the colloid.

2354 Such adsorption of ions upon the surface of solids in solution is largely, but not entirely, based  
2355 upon electrical attraction, otherwise adsorption would not be selective. Recall that there are four  
2356 other factors, in addition to magnitude of charge, that affect the preferential adsorption by a  
2357 colloid (see *Surface Adsorption* in Section 14.8.4.1, “Coprecipitation Process”).

2358 • The Paneth-Fajans-Hahn Law dictates that when two or more types of ions are available for  
2359 adsorption, the ion that forms the least soluble compound with one of the lattice ions will be  
2360 adsorbed preferentially.

2361 • The ion present in the greater concentration will be adsorbed preferentially.

2362 • Ions with a large radius will be adsorbed more readily than ions with a smaller radius because  
2363 the larger ion is less hydrated by the solution and not as attracted to the solution phase.

2364 • The ion that is closer to the same size as the lattice ion will be adsorbed preferentially. For  
2365 example, radium ions are adsorbed tightly onto barium sulfate, but not onto calcium sulfate;  
2366 radium ions are close in size to barium ions, but are much larger than calcium ions.

2367 If an excess of electrolyte is added to the colloidal solution, the electrical double layer is  
2368 destroyed and the particles can agglomerate to form larger particles that can settle to the bottom  
2369 of the container, a process known as *flocculation* (or *coagulation*). For example, Smith et al.  
2370 (1995) used polyethylene glycol to remove colloidal silica from a dissolved-soil solution before  
2371 the addition of the sample to an ion-exchange resin. Alternatively, the process whereby  
2372 coagulated particles pass back into the colloidal state is known as *deflocculation*, (or *peptiza-*  
2373 *tion*). Special precautions should be taken during the washing of coagulated precipitates to assure  
2374 that deflocculation does not occur. When coagulation is accomplished through charge  
2375 neutralization, deflocculation would occur if the precipitate was washed with water. A solution  
2376 containing a volatile electrolyte such as nitric acid should be used instead.

2377 There are two types of colloidal solutions (Salutsky, 1959, p. 744):

2378 • *Hydrophobic colloids* show little or no attraction for water. These solutions have a low  
2379 viscosity, can be easily flocculated by the addition of an appropriate electrolyte, and yield  
2380 precipitates that are readily filterable.

- 2381 • *Hydrophilic colloids* have a high affinity for water and are often highly viscous. They are  
2382 more difficult to flocculate than hydrophobic colloids, and relatively large amounts of  
2383 electrolytes are necessary to cause precipitation. The flocculate keeps water strongly adsorbed  
2384 and tends to form jellylike masses that are difficult to filter.

2385 Colloidal precipitations can be a useful separation technique. Because of their great adsorption  
2386 capacity, colloidal precipitates are excellent *scavengers (collectors)* for concentrating trace  
2387 substances (Salutsky, 1959, p. 747). Unspecific carriers such as manganese dioxide, sulfides and  
2388 hydrated oxides are frequently used as scavengers. For example, protactinium can be efficiently  
2389 scavenged and concentrated on manganese dioxide that is precipitated by adding a manganous  
2390 salt to a solution containing permanganate. Ferric hydroxide is commonly used to scavenge  
2391 cations (Section 14.8.4.4, “Coprecipitation Methods”). Moreover, scavenging precipitations can  
2392 sometimes be used to remove interferences. For example, a radionuclide that is capable of  
2393 existing in two oxidation states can be effectively purified by precipitation in one oxidation state,  
2394 followed by scavenging precipitations for impurities, while the element of interest is in another  
2395 oxidation state. A useful procedure for cerium purification involves repeated cycles of ceric  
2396 iodate precipitation, reduction to  $Ce^{+3}$ , zirconium iodate ( $ZrIO_3$ ) precipitation to remove  
2397 impurities (with  $Ce^{+3}$  staying in solution), and reoxidation to  $Ce^{+4}$ .

#### 2398 **14.8.6 Filterability of Precipitates**

2399 The physical nature of a precipitate not only affects the purity of the precipitate, but also the  
2400 filterability of the precipitate. Large, well-formed crystals are desirable because they tend to  
2401 contain fewer impurities, and are also easier to filter and wash. Many coagulated colloidal  
2402 precipitates, such as hydrous oxides or sulfides, tend to form slimy aggregates and to clog the  
2403 filter during filtration. There are several approaches that can be taken to improve the physical  
2404 form of the precipitate (Salutsky, 1959, pp. 758-761):

- 2405 • A trace quantity of a hydrophilic colloid can be added to produce complete and rapid  
2406 flocculation. For example, gelatin has been used as a *sensitizer* in the precipitation of zinc  
2407 sulfide, hydrous silica, and various other hydrous oxides, as well-coagulated, filterable  
2408 precipitates (Salutsky, 1959, p. 759).
- 2409 • The slow precipitation techniques described in Section 14.8.3.2, “Factors Affecting  
2410 Precipitation,” can be used to produce good precipitates.
- 2411 • Aging the precipitate can result in a precipitate more amenable to filtration. During *aging*,  
2412 small particles with a larger solubility go into solution, and larger particles grow at the cost of

2413 the smaller ones (see “Digestion” under Section 14.8.3.2, “Factors Affecting Precipitation”).  
 2414 Ostwald ripening results in a decrease in the number of particles and, therefore, a decrease in  
 2415 surface area. The speed of aging generally increases with temperature and with the increasing  
 2416 solubility of the precipitate in the aging media. Shaking can sometimes promote aging,  
 2417 perhaps by allowing particles to come into contact and to cement together.

2418 Table 14.15 summarizes general properties of common filters used in analytical procedures.

2419 **TABLE 14.15 — General properties of common filter papers** <sup>(1)</sup>

Whatman Grade	Particle Retention (µm)	Porosity	Ash (%)	Filter speed	Applications
Qualitative filter papers					
1	> 11	Medium	0.06	Medium-fast	Medium crystalline precipitates. A general purpose filter used in routine laboratory applications, air pollution monitoring, and soil chemical assays.
2	> 8	Medium-fine	0.06	Medium	Crystalline precipitates. More retentive and adsorbent than Grade 1, but with increased filtering time.
3	> 6	Medium-fine	0.06	Medium	Double the thickness of Grade 1 for high precipitate capacity and increased wet strength. Suitable for suction filtration.
4	> 20-25	Coarse	0.06	Fast	Coarse and gelatinous precipitates. Used in air pollution monitoring and for routine cleanup of biological fluids.
5	> 2.5	Fine	0.06	Slow	Fine crystalline precipitates. Most retentive of the series, and is useful for clarifying cloudy suspensions and water analysis.
6	> 3	Fine	0.2	Slow	Fine crystalline precipitates. Twice as fast as Grade 5. Often specified in boiler water analyses.
Quantitative – ashless					
40	> 8	Medium	0.010	Medium	Medium crystalline precipitates: calcium oxalate, well-digested barium. Widely used, general purpose.
41	> 20-25	Coarse	0.010	fast	Gelatinous precipitates and coarse particles: iron and aluminum hydroxides. Also used in quantitative air analyses.
42	> 2.5	Medium	0.010	Slow	Highly retentive for fine particles. The laboratory standard for critical gravimetric analysis.

Whatman Grade	Particle Retention (µm)	Porosity	Ash (%)	Filter speed	Applications	
2433	43	> 16	Medium	0.010	Medium-fast	Medium crystalline precipitates. Foodstuff and soil analyses, particle collection in air pollution monitoring by XRF.
2434	44	> 3	Fine	0.010	Slow	Fine crystalline precipitates. Somewhat thinner and faster than Grade 42.
Quantitative – hardened low ash						
2435	50	> 2.7	Fine	0.025	Slow	Hardened papers are designed for use in Buchner funnels, possess great wet strength and lintless surfaces, and will withstand scraping. Grade 50: fine crystalline precipitates. Grade 52: crystalline precipitates, general purpose filtration. Grade 54: gelatinous precipitates and coarse particles.
2436	52	> 7	Medium	0.025	Medium	
2437	54	> 20-25	Coarse	0.025	Fast	
2438	Quantitative – hardened ashless					
2439	540	> 8	Medium	0.008	Medium	Crystalline precipitates. Gravimetric analysis of metals in acid/alkali solutions. Collecting hydroxides after precipitation from strong alkali solutions.
2440	541	> 20-25	Coarse	0.008	Fast	Coarse gelatinous precipitates. Used for strongly acidic or alkaline conditions.
2441	542	> 2.7	Fine	0.008	Slow	Fine crystalline precipitates from under demanding acidic/alkali conditions.

(1) Fisher (2000-01)

### 14.8.7 Advantages and Disadvantages of Precipitation and Coprecipitation

#### Advantages

- Provides the only practical method of separation or concentration in some cases.
- Can be highly selective and virtually quantitative.
- High degree of concentration is possible.
- Provides a large range of scale (mg to industrial).
- Convenient, simple process.
- Carrier can be removed and procedure continued with tracer amounts of material (e.g., carrier iron separated by solvent extraction).

#### Disadvantages

- Can be time consuming to digest, filter, and/or wash the precipitate.
- Precipitate can be contaminated by carrying of ions or postprecipitation.
- Large amounts of carrier might interfere with subsequent separation procedures.
- Coprecipitating agent might contain isotopic impurities of the analyte radionuclide.
- Scavenger precipitates are not as selective and are more sensitive to changes in separation procedures.

2455 **14.9 Carriers and Tracers**2456 **14.9.1 Introduction**

2457 Radiochemical analysis frequently requires the radiochemist to separate and determine  
 2458 radionuclides that are present at extremely small quantities. The amount can be in the picomole  
 2459 range or less, at concentrations in the order of  $10^{-15}$  to  $10^{-11}$  molar. Analysis of radionuclides  
 2460 using counting techniques, such as alpha spectrometry, liquid scintillation, proportional counting,  
 2461 or gamma spectrometry, allows activities of radionuclides of 10,000 disintegrations per minute  
 2462 (dpm) to be determined easily, even though the number of atoms (and mass percent) of these  
 2463 materials is vanishingly small. Table 14.16 identifies the number of atoms and mass present in  
 2464 several radionuclides, based on an activity of 500 dpm.

2465 **TABLE 14.16 — Atoms and mass of select radionuclides equivalent to 500 dpm<sup>(1)</sup>**

Radionuclide	Half-life	Number of Atoms	Mass (g)
Radium-226	1590 y	$6.0 \times 10^{11}$	$2.3 \times 10^{-10}$
Polonium-210	140 d	$1.5 \times 10^8$	$5.0 \times 10^{-14}$
Lead-212	10.6 h	$4.5 \times 10^5$	$1.6 \times 10^{-16}$
Thallium-208	3.1m	$2.3 \times 10^3$	$8.0 \times 10^{-19}$

2470 (1) Based on Wahl and Bonner, 1951, p. 102

2472 Considering the minute masses of these analytes and their subsequently low concentration in  
 2473 solution, it is obvious why conventional techniques of analysis, such as gravimetry, spectro-  
 2474 photometry, titrimetry, and electrochemistry, cannot be used for their quantitation. However, it is  
 2475 not immediately obvious why these small quantities might present other analytical difficulties.  
 2476 As described below, the behavior of such small quantities of materials can be seriously affected  
 2477 by macro constituents in an analytical mixture in a way that may be unexpected chemically.

2478 **14.9.2 Carriers**

2479 The key to radiochemical analysis of samples with multiple radionuclides is effective separation  
 2480 of the different analytes. Separations are most easily accomplished when performed on a macro  
 2481 scale. As described above, however, the analytes are frequently at levels that challenge the  
 2482 analyst and the conventional methods to perform the separations. The use of a material that is  
 2483 different in isotopic make-up to the analyte and that raises the effective concentration of the  
 2484 material to the macro level is referred to as a *carrier*. In many cases, the carrier is a non-  
 2485 radioactive isotope of the analyte. Some carriers are stable isotopes of chemically similar  
 2486 elements.

2487 A distinction exists between traditional and radiochemical analyses when referring to macro  
2488 amounts. Generally, carriers are present in quantities from a few tenths to several hundred  
2489 milligrams of material during the progress of the radiochemical separation.

2490 14.9.2.1 Isotopic Carriers

2491 An isotopic carrier is usually a stable isotope of the analyte. Stable strontium (consisting of  
2492 naturally occurring  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$ , and  $^{88}\text{Sr}$ ) is frequently used as the carrier in the analysis of  $^{89}\text{Sr}$   
2493 and  $^{90}\text{Sr}$ . Regardless of the stability of the isotope, the number of protons in the nucleus  
2494 ultimately governs the chemical properties of the isotope. Thus, all nuclei that have 38 protons  
2495 are strontium and react as strontium classically does.

2496 The purpose of adding a carrier is to raise the chemical concentration of the analyte to the point  
2497 where it can be separated using conventional techniques, but for the carrier to perform properly,  
2498 it must have the same oxidation state and chemical form as the analyte. It is important then to add  
2499 the carrier to the sample as early as possible in chemical process. For example, in the determina-  
2500 tion of  $^{131}\text{I}$  in milk, the radioiodine might be present as  $\text{I}^-$ ,  $\text{IO}_3^-$ ,  $\text{CH}_3\text{I}$ , or  $\text{I}_2$ . The analyst should  
2501 assume that all states are present, and treat the sample so that all atoms are brought to a common  
2502 oxidation state and chemical form during some step in the procedure, before any separation takes  
2503 place. If the final step is precipitation of  $\text{AgI}$  and the carrier is in the  $\text{IO}_3^-$  form, no precipitate  
2504 will form since  $\text{AgIO}_3$  that forms when  $\text{Ag}^+$  is added is relatively soluble compared to  $\text{AgI}$ .  
2505 Furthermore, if separations of other radioisotopes are performed before this step, there is the  
2506 possibility that quantities of the radioiodine could be trapped in the precipitate with other  
2507 separated analytes. When concentrations of these materials are very small, even small losses are  
2508 significant. The carrier also functions to prevent losses of the analyte during the separation of  
2509 other radionuclides or interfering macro-contaminants. This is another reason that it is essential  
2510 to add the carrier prior to any chemical treatment of the sample.

2511 The laws of equilibrium for precipitation, distillation, complexation, and oxidation-reduction will  
2512 apply to the entire chemical form of analyte in solution, both carrier and radioisotope. If, for  
2513 example, 99.995 percent of all strontium is determined to be precipitated during a radiochemical  
2514 procedure, then the amount of stable strontium remaining in solution will be 0.005 percent,  
2515 which means that 0.005 percent of the radiostrontium still remains in the solution as well. Losses  
2516 such as this occur during any chemical process. Frequently then, carriers are used in radiochemi-  
2517 cal analyses not only to raise the chemical concentration of the element, but also to determine the  
2518 yield of the process. In order to determine the exact amount of radionuclide that was originally  
2519 present in the sample, the yield (sometimes called the recovery) of the radionuclide collected at  
2520 the end of the procedure should be known. However, since the amount of analyte at the start of

2521 the procedure is the unknown, the yield should be determined by an alternate method. The mass  
2522 of the radioanalyte is insignificant in comparison to the carrier, and measuring the yield of the  
2523 carrier (gravimetrically, for example) will allow the calculation of the yield of the analyte.

#### 2524 14.9.2.2 Nonisotopic Carriers

2525 Non-isotopic carriers are materials that are similar in chemical properties to the analyte being  
2526 separated, but do not have the same number of protons in their nucleus. Usually these carriers  
2527 will be elements in the same family in the periodic table. In the classical separation of radium by  
2528 the Curies, the slight difference in solubility of radium chloride versus barium chloride allowed  
2529 the tedious fractional crystallization of radium chloride to take place (Hampel, 1968, p. 586).  
2530 When barium is present in macro-quantities and the radium in femtogram quantities, however,  
2531 the two may be easily precipitated together as a sulfate.

2532 For several elements, non-isotopic carriers are chosen from a different family of elements, but  
2533 they have the same ionic charge or similar crystalline morphology as the analyte. Lanthanum and  
2534 neodymium as +3 ions are frequently used as nonisotopic carriers for U(IV) and Pu(IV) in their  
2535 final separation as insoluble fluorides by the process of coprecipitation (Metz and Waterbury,  
2536 1962, p. 254) (see also Section 14.8, "Precipitation and Coprecipitation"). The chemical form of  
2537 the uranium and plutonium is particularly important for this process; the +4 oxidation state will  
2538 coprecipitate, but the +6 in the  $\text{MO}_2^{+2}$  form, will not. Uranium(IV) is present in solution as  $\text{UO}_2^{+2}$   
2539 and, therefore, will not be coprecipitated with lanthanum fluoride. However, it is very important  
2540 to note that even though the precipitation of  $\text{LaF}_3$  may be quantitative (i.e., >99.995 percent may  
2541 be precipitated), there is no measure of how much uranium will also be coprecipitated. Since  
2542 uranium and plutonium are not chemically equivalent, the laws of solubility product constant for  
2543 lanthanum cannot be applied to uranium. For these types of processes, separate methods should  
2544 be used to determine the chemical yield of the process.

2545 For alpha counting rare earths, fluorides (such as  $\text{NdF}_3$ ) are frequently used to coprecipitate  
2546 elements (Hindman, 1983 and 1986; Sill and Williams, 1981).

2547 Another group of non-isotopic carriers can be described as general scavengers. Substances with  
2548 high surface areas, or the ability to occlude contaminants in their floc, can be used to effect gross  
2549 separation of all radionuclides from macro quantities of interfering ions. Ferric hydroxide,  
2550 manganese dioxide ( $\text{MnO}_2$ ) and sulfides ( $\text{MnS}$ ), and hydrated oxides [ $\text{Mn}(\text{OH})_x$ ] are examples of  
2551 these nonspecific carriers that have been used in many radiochemical separations to eliminate  
2552 gross quantities of interfering substances.

2553 14.9.2.3 Common Carriers

2554 Carriers for specific analytes are discussed below.

2555 Alkaline Earths

2556 STRONTIUM AND BARIUM. Carrier-free strontium ( $\text{Sr}^{2+}$ ) and barium ( $\text{Ba}^{2+}$ ) will coprecipitate with  
2557 ferric hydroxide [ $\text{Fe}(\text{OH})_3$ ], while calcium ( $\text{Ca}^{2+}$ ) exhibits the opposite behavior and does not  
2558 coprecipitate with ferric hydroxide. Lead sulfate ( $\text{PbSO}_4$ ) will also carry strontium and barium.

2559 Frequently, inactive strontium and barium are used as carriers for the radionuclides in order to  
2560 facilitate separation from other matrix constituents and from calcium. The precipitates used most  
2561 frequently in radiochemical procedures are the chromates ( $\text{CrO}_4^{2-}$ ), nitrates ( $\text{NO}_3^{-1}$ ), oxalates  
2562 ( $\text{C}_2\text{O}_4^{2-}$ ), sulfates ( $\text{SO}_4^{2-}$ ), and barium chloride ( $\text{BaCl}_2$ ). Several different methods of separation  
2563 are identified here:

- 2564 • Chromate precipitation is used in the classical separation of the alkaline earths. Barium  
2565 chromate ( $\text{BaCrO}_4$ ) is precipitated from a hot solution buffered to a pH of 4 to minimize  
2566 strontium and calcium contamination of the barium precipitate. Ammonium ion ( $\text{NH}_4^{+1}$ ) is  
2567 then added to the solution, and strontium chromate ( $\text{SrCrO}_4$ ) is precipitated.
- 2568 • Barium and strontium can be separated from calcium as the nitrates. Fuming nitric acid is  
2569 used to increase the nitric acid concentration to 60 percent, conditions at which barium and  
2570 strontium nitrate [ $\text{Ba}(\text{NO}_3)_2$  and  $\text{Sr}(\text{NO}_3)_2$ ] precipitate and calcium does not.
- 2571 • Oxalate precipitation does not separate one alkaline earth from another, but it is usually used  
2572 to produce a weighable and reproducible form suitable for radioassay. The precipitation is  
2573 accomplished from a basic solution with ammonium oxalate [ $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ].
- 2574 • Barium sulfate ( $\text{BaSO}_4$ ) precipitation is generally not used in separation procedures. It is  
2575 more common as a final step to produce a precipitate that can be readily dried, weighed, and  
2576 mounted for counting. Barium is readily precipitated by slowly adding dilute sulfuric acid  
2577 ( $\text{H}_2\text{SO}_4$ ) to a hot barium solution and digesting the precipitate. For the precipitation of  
2578 strontium or calcium sulfate ( $\text{SrSO}_4$  and  $\text{CaSO}_4$ ), a reagent such as alcohol should be added to  
2579 lower the solubility, and the precipitant must be coagulated by heat.
- 2580 • Insolubility of barium chloride ( $\text{BaCl}_2$ ) in strong hydrochloric acid solution ( $\text{HCl}$ ) is the basis  
2581 of the method to separate barium from calcium, strontium, and other elements. The

2582 precipitation is performed either by adding an ether-hydrochloric acid solution or by bubbling  
2583 dry hydrogen chloride gas into the aqueous solution.

2584 RADIUM. Radium (Ra) yields the same types of insoluble compounds as barium: sulfates,  
2585 chromates, carbonates ( $\text{CO}_3^{-2}$ ), phosphates ( $\text{PO}_4^{-3}$ ), oxalates, and sulfites ( $\text{SO}_3^{-2}$ ). Hence, radium  
2586 coprecipitates with all barium compounds and, to a lesser extent, with most strontium and lead  
2587 compounds. Barium sulfate and barium chromate are most frequently used to carry radium. Other  
2588 compounds that are good carriers for radium include ferric hydroxide when precipitated at  
2589 moderately high pH with sodium hydroxide (NaOH), barium chloride when precipitated from a  
2590 cold mixed solvent of water and alcohol saturated with hydrochloric acid, barium iodate ( $\text{BaIO}_3$ )  
2591 and various insoluble phosphates, fluorides ( $\text{F}^{-1}$ ) and oxalates (e.g., thorium phosphate  
2592 [ $\text{Th}_3(\text{PO}_4)$ ], lanthanum fluoride ( $\text{LaF}_3$ ), and thorium oxalate [ $\text{Th}(\text{C}_2\text{O}_4)$ ].

2593 Rare Earths, Scandium, Yttrium, and Actinium

2594 Ferric hydroxide and calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) will coprecipitate carrier-free rare earths without  
2595 difficulty.

2596 The rare earths will coprecipitate one with another in almost all of their reactions; one rare earth  
2597 can always be used to coprecipitate another. The rare earth hydroxides, fluorides, oxalates, and 8-  
2598 hydroxyquinolates in ammoniacal solution are insoluble. Conversely, the rare earth hydroxides  
2599 will carry a number of elements that are insoluble in basic solution; the rare earth oxalate will  
2600 coprecipitate calcium; and the rare earth fluorides tend to carry barium and zirconium (Zr). In the  
2601 absence of macro quantities of rare earths, actinium will carry on barium sulfate and lead sulfate  
2602 ( $\text{PbSO}_4$ ).

2603 Lead

2604 Ferric hydroxide and aluminum hydroxide [ $\text{Al}(\text{OH})_3$ ] carry lead very effectively from ammonium  
2605 solutions under a variety of conditions. Lead is carried by barium or radium chloride, but not  
2606 carried by barium or radium bromide ( $\text{BaBr}_2$  or  $\text{RaBr}_2$ ). This behavior has been used to separate  
2607 radilead isotopes from radium salts. Lead is also carried by barium carbonate ( $\text{BaCO}_3$ ), barium  
2608 sulfate, radium sulfate, radium chloride, lanthanum carbonate [ $\text{La}_2(\text{CO})_3$ ], barium chloride, and  
2609 silver chromate ( $\text{Ag}_2\text{CrO}_4$ ). Calcium sulfate in the presence of alcohol has also been used to  
2610 coprecipitate lead.

2611 Polonium

2612 Trace quantities of polonium (Po) are carried almost quantitatively by bismuth hydroxide  
2613 [Bi(OH)<sub>3</sub>] from ammoniacal solution. Ferric, lanthanum, and aluminum hydroxides have also  
2614 been used as carriers for polonium in alkaline solutions. Colloidal platinum and coagulated silver  
2615 hydroxide (AgOH) and ferric hydroxide sols have been used to carry polonium. Because of the  
2616 high oxidation state of polonium, it is susceptible to being a contaminant in almost any  
2617 precipitate. Removal of polonium by electrodeposition on nickel metal is recommended prior to  
2618 final precipitation for any gross counting technique (proportional counting and liquid  
2619 scintillation, for example).

2620 Actinides

2621 THORIUM. Thorium (Th) will coprecipitate with ferric, lanthanum [La(OH)<sub>3</sub>], and zirconium  
2622 hydroxide [Zr(OH)<sub>4</sub>]. These hydroxide carriers are nonspecific, and therefore, will only remove  
2623 thorium from a simple group of contaminants or as a group separation. The ferric hydroxide  
2624 precipitation is best carried out at pH 5.5-6.

2625 Thorium will coprecipitate quantitatively with lanthanum fluoride from strongly acidic solutions,  
2626 providing an effective means to remove small quantities of thorium from uranium solutions.  
2627 However, the rare earths will also carry quantitatively, and zirconium and barium radioisotopes  
2628 will carry unless macro quantities of these elements are added as holdback carriers (see Section  
2629 14.9.2.4, "Holdback Carriers").

2630 Precipitation of thorium with barium sulfate is possible from strongly acidic solutions containing  
2631 high concentrations of alkali metal sulfates; however, this coprecipitation is nonspecific. Other  
2632 actinides, lead, strontium, rare earths, bismuth, scandium (Sc), and yttrium will also carry.

2633 Coprecipitation of thorium on hydrogen hypophosphate (HPO<sub>3</sub><sup>-2</sup>) or phosphate carriers can be  
2634 performed from rather strongly acidic solutions. Zirconium phosphate [Zr<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>] serves as a  
2635 good carrier for trace levels of thorium. Moreover, thorium also will carry quantitatively on  
2636 zirconium iodate from a strongly acidic solution. If coprecipitation is performed from a strongly  
2637 acidic solution and the precipitate is washed with a solution containing iodate, the rare earths and  
2638 actinium are eliminated. Ce<sup>+4</sup> must be reduced to Ce<sup>+3</sup> before precipitation so that it does not  
2639 carry.

2640 PROTACTINIUM. Protactinium will be carried quantitatively on hydroxide, carbonate, or  
2641 phosphate precipitates of tantalum (Ta), zirconium, niobium (Nb), hafnium (Hf), and titanium

2642 (Ti). It is also carried by adsorption onto flocculent precipitates of calcium hydroxide [Ca(OH)<sub>2</sub>]  
2643 or ferric hydroxide, and it is carried by manganese dioxide, which is produced by addition of  
2644 potassium permanganate (KMnO<sub>4</sub>) to a dilute nitric acid (HNO<sub>3</sub>) solution containing manganese  
2645 nitrate. However, titanium and zirconium are also carried under these conditions.

2646 URANIUM. Trace concentrations of uranium can be coprecipitated with any of the common  
2647 insoluble hydroxides. When coprecipitating U(VI) with hydroxides at pH 6-7, the ammonium  
2648 used must be free of carbonate or some of the uranium will remain in solution as the stable  
2649 anionic carbonate complex. Hydroxide precipitation is nonspecific, and many other metals will  
2650 carry with the uranium.

2651 Uranium(IV) can be coprecipitated as the fluoride or phosphate [UF<sub>4</sub> or U<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>] from relatively  
2652 strong acid media; however, U(VI) phosphate [(UO<sub>2</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>] is precipitated only from very weak  
2653 acid solutions (pH 5-6) by the addition of carbonate-free ammonium. The rare earths, and other  
2654 metals can also coprecipitate under these conditions.

2655 In general, U<sup>+4</sup> should behave similarly to Pu<sup>+4</sup> and Np<sup>+4</sup>, and should be carried by lanthanum  
2656 fluoride, ceric and zirconium iodates [Ce(IO<sub>4</sub>)<sub>3</sub> and Zr(IO<sub>4</sub>)<sub>4</sub>], cerium and thorium oxalates  
2657 [Ce<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>], barium sulfate, zirconium phosphate [Ce<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>], and bismuth arsenate (BiAsO<sub>4</sub>).  
2658 However, U(VI) does not carry with these agents as long as the concentration of either carrier or  
2659 that of uranium is not too high.

2660 PLUTONIUM AND NEPTUNIUM. Classically, plutonium (Pu) and neptunium (Np) in their ter- and  
2661 tetravalent oxidation states have been coprecipitated with lanthanum fluoride in the method most  
2662 widely used for the isolation of femtograms of plutonium. However, large amounts of aluminum  
2663 interfere with coprecipitation of plutonium, and other insoluble fluorides, such as the rare earths,  
2664 calcium, and U<sup>+4</sup>, coprecipitate.

2665 AMERICIUM AND CURIUM. Bismuth phosphate (BiPO<sub>4</sub>), which historically has been used to  
2666 precipitate plutonium, will also carry americium and curium from 0.1-0.3 M nitric acid.  
2667 Impurities such as calcium and magnesium are not carried under these conditions.

2668 Lanthanum fluoride provides a convenient carrier for Am<sup>+3</sup> and Cm<sup>+3</sup>. A lanthanum fluoride  
2669 precipitation is not totally specific, but it can provide a preliminary isolation from the bulk of the  
2670 fission products and uranium. Additionally, a lanthanum fluoride precipitation can be used to  
2671 separate americium from curium. Am<sup>+3</sup> is oxidized to Am(V) in dilute acid with persulfate, and  
2672 fluoride is added to precipitate Cm<sup>+3</sup> on lanthanum fluoride.

2673 14.9.2.4 Holdback Carriers

2674 It is often necessary to add holdback carriers to analytical mixtures to prevent unwanted  
2675 radionuclides from being carried in a chemical process. Coprecipitation of a radionuclide with  
2676 ferric hydroxide carries other ions in addition to the analyte, because of its tendency to adsorb  
2677 other ions and occlude them in its crystal matrix. The addition of a holdback carrier, a highly-  
2678 charged ion, such as  $\text{Co}^{+3}$ , represses counter-ion exchange and adsorption to minimize the  
2679 attraction of foreign ions. The amount of a given substance adsorbed onto a precipitate depends  
2680 on its ability to compete with other ions in solution. Therefore, ions capable of displacing the  
2681 radionuclide ions (the hold-back carrier) are added to prohibit the coprecipitation of the  
2682 radionuclide. Highly charged ions, chemical homologs, and ions isotopic with the radionuclide  
2683 are among the most efficient holdback carriers. Hence, the addition of inactive strontium makes  
2684 it possible to precipitate radiochemically pure radiobarium as the nitrate or chloride in the  
2685 presence of radiostrontium. Actinium and the rare earth elements can be separated from  
2686 zirconium and radium by lanthanum fluoride coprecipitation with the addition of zirconium and  
2687 barium holdback carriers. Holdback carriers are used in other processes as well. The extraction of  
2688 lutetium from water employs neodymium ions ( $\text{Nd}^{+3}$ ) to avoid adsorption losses (Choppin et al.,  
2689 1995, p. 262).

2690 14.9.2.5 Yield (Recovery) of Isotopic Carriers

2691 The use of an isotopic carrier to determine the chemical yield of the analyte is a critical step in  
2692 the plan of a radiochemical analysis. The analytical method being used to determine the final  
2693 amount of carrier will govern the method of separation. If a gravimetric method is to be used for  
2694 the final yield determination, the precipitate must have all the characteristics that would be used  
2695 for macro gravimetric analysis—easily dried, definite stoichiometry, non-hygroscopic, and the  
2696 like.

2697 Similarly, the reagent used as source of carrier at the beginning of the analysis must be of  
2698 primary-standard quality to ensure that the initial mass of carrier added can be determined very  
2699 accurately. For a gravimetric yield determination, the equation would be the following:

2700 
$$\text{Percent Yield} = \frac{(\text{mass of carrier in final separation step}) \times 100\%}{(\text{mass of carrier added})}$$
  
2701

2702 It should be recognized that the element of interest is the only quantity used in this formula. For  
2703 example, if strontium nitrate is used as the primary standard and strontium sulfate is the final

2704 precipitate, both masses should be corrected, using a gravimetric factor, so that only the mass of  
2705 strontium is used in the equation in both the numerator and denominator.

2706 Other methods to determine the yield of the carrier include atomic absorption spectrometry, ultra-  
2707 violet/visible spectrometry, titrimetry, and potentiometry.

### 2708 **14.9.3 Tracers**

2709 The term *tracer* was classically used to express the concentration of any pure radionuclide in  
2710 solution that had a mass too small to be measured by an analytical balance (<0.0001 to  
2711 0.00001 g). More recently, the definition of a tracer has become more pragmatic. The current  
2712 definition of a tracer is a known quantity of a radioisotope that is added to a solution of a  
2713 chemically equivalent radioisotope of unknown concentration so that the yield of the chemical  
2714 separation can be monitored. In general, a tracer is not a carrier, and a carrier is not a tracer.

2715 The analysis of  $^{241}\text{Am}$  in an environmental sample provides an example of a radioisotope  
2716 employed in a manner consistent with the recent use of the term *tracer*. In the analytical  
2717 procedure, no stable isotope of americium exists to act as a carrier. Femtogram quantities of  
2718  $^{243}\text{Am}$  can be produced, however, with accurately known activities. If a known quantity of  $^{243}\text{Am}$   
2719 in solution is added to the unknown sample containing  $^{241}\text{Am}$  at the beginning of the separation  
2720 procedure, and if the resulting activity of  $^{243}\text{Am}$  can be determined at the end of the procedure,  
2721 then the yield of  $^{241}\text{Am}$  can be determined accurately for the process.  $^{243}\text{Am}$  added to the sample  
2722 in this example is used as a tracer. A measurable mass of this element was not used, but a known  
2723 activity was added through addition of the solution. During the course of the radiochemical  
2724 separation, lanthanides may have been used to help carry the americium through analysis.  
2725 However, they are not used to determine the yield in this example and would be considered,  
2726 therefore, a non-isotopic carrier.

2727 When using a tracer in an analytical method, it is important to consider the availability of a  
2728 suitable isotope, its chemical form, its behavior in the system, the amount of activity required, the  
2729 form in which it should be counted, and any health hazards associated with it (McMillan, 1975,  
2730 p. 298).

2731 Perhaps the most important property of the tracer is its half-life. It is preferable to select an  
2732 isotope with a half-life that is long compared to the duration of the experiment. By doing so, one  
2733 avoids the problems of having to handle high levels of activity at the beginning of the experiment  
2734 and of having to make large decay corrections.

2735 Purity of the tracer is of critical importance. Radionuclide and radiochemical impurities are the  
2736 two principal types of impurities encountered. Radionuclide impurity refers to the presence of  
2737 radionuclides other than those desired. For instance, it is very difficult to obtain  $^{236}\text{Pu}$  tracer that  
2738 does not contain a very small quantity of  $^{239}\text{Pu}$ . This impurity should be taken into account when  
2739 calculating the  $^{239}\text{Pu}$  activity levels of samples. Radiochemical impurity refers to the nuclide of  
2740 interest being in an undesired chemical form. This type of impurity has its largest effects in  
2741 organic tracer studies, where the presence of a tracer in the correct chemical form is essential. For  
2742 example, the presence of  $^{32}\text{P}$ -labeled pyrophosphate in an orthophosphate tracer could lead to  
2743 erroneous results in an orthophosphate tracer study.

2744 Tracer solutions can also contain other forms of radiochemical impurities. Many tracers are  
2745 actinides or other isotopes that have progeny that are radioactive. Tracer solutions are purchased  
2746 with known specific activities for the isotopes listed in the solutions. However, from the time of  
2747 production of the tracer, ingrowth of progeny radioisotopes occurs.  $^{236}\text{Pu}$  is used as a tracer for  
2748  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  analysis, for example.  $^{236}\text{Pu}$  has a half-life of 2.9 years and decays to  $^{232}\text{U}$ , which  
2749 has a half-life of 72 years. After solutions of  $^{236}\text{Pu}$  have been stored for about three years, half of  
2750 the radionuclide will be converted to  $^{232}\text{U}$ . If the solution is then used as a tracer in a procedure  
2751 for analysis of uranium and plutonium in soil, erroneously high results would be produced for the  
2752 content of uranium if a gross-counting technique is used. Thus, it is important to consider  
2753 chemical purification of a tracer solution prior to use to remove unwanted radioactive progeny.

2754 Tracer analysis is very dependent upon the identical behavior of the tracer and the analyte.  
2755 Therefore, tracers should be added to the system as early as possible, and complete isotopic  
2756 exchange should be ensured as discussed previously (see Section 14.10, "Radiochemical  
2757 Equilibrium"). Obvious difficulties arise when a tracer is added to a solid sample, especially if  
2758 the sample is subdivided. Unless complete dissolution and isotopic exchange is ensured, results  
2759 should be interpreted carefully.

2760 Isotopes selected for tracer work should be capable of being easily measured. Gamma-emitting  
2761 isotopes are ideal because they can easily be detected by gamma spectroscopy without being  
2762 separated from other matrix constituents. Alpha- and beta-emitting tracers require separation  
2763 before counting. Some common tracers are listed below:

- 2764 •  $^{85}\text{Sr}$  has a 514 KeV gamma ray that can be used to monitor the behavior of strontium in a  
2765 system, or for yield determination in a  $^{89}\text{Sr}/^{90}\text{Sr}$  procedure, as long as the gamma is accounted  
2766 for in the beta-counting technique.

- 2767 •  $^{99m}\text{Tc}$  with a half-life of 6.02 h and a 143 KeV gamma ray is sometimes used as a yield  
 2768 monitor for  $^{99}\text{Tc}$  determinations. Samples are counted immediately to determine the chemical  
 2769 recovery, then the  $^{99m}\text{Tc}$  is allowed to decay before analysis of the  $^{99}\text{Tc}$ .
- 2770 •  $^{152}\text{Eu}$  and  $^{145}\text{Sm}$  are frequently used in the development of a new method to estimate the  
 2771 behavior of the +3 actinides and lanthanides.
- 2772 •  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{32}\text{P}$ , and  $^{36}\text{Cl}$  are frequently used in biological studies. In some of these studies, the  
 2773 radionuclide is covalently bonded to a molecule. As a result, the chemical behavior of the  
 2774 radionuclide will follow that of the molecule, not the element.
- 2775 •  $^{229}\text{Th}$  is used for Th determinations, both in alpha spectroscopy and inductively coupled  
 2776 plasma-mass spectroscopy (ICP-MS).
- 2777 •  $^{232}\text{U}$  is commonly used as a tracer in alpha spectroscopy, whereas  $^{236}\text{U}$  is used for ICP-MS  
 2778 determinations. It should be noted that  $^{232}\text{U}$  decays to  $^{228}\text{Th}$  and therefore needs to be taken  
 2779 into account if determining Th isotopes in the same sample.
- 2780 •  $^{242}\text{Pu}$  and  $^{236}\text{Pu}$  are both used as tracers in Pu analyses. However,  $^{236}\text{Pu}$  decays to  $^{232}\text{U}$ , which  
 2781 needs to be taken into account when analyzing both Pu and U in the same sample aliquant.
- 2782 •  $^{243}\text{Am}$  is employed in the analysis of  $^{241}\text{Am}$  and Cm by alpha spectroscopy. It is assumed that  
 2783 Am and Cm are displaying similar chemical behavior.

2784 14.9.3.1 Characteristics of Tracers

2785 The behavior of tracers is often different from that of elements in normal concentrations. The  
 2786 chemical form of a radionuclide predominant at normal concentrations, for example, might not  
 2787 be the primary form at tracer concentrations. Alternatively, a shift in the equilibrium that is partly  
 2788 responsible for a radionuclide's chemical behavior might increase or reduce its concentration as a  
 2789 result of the low tracer concentration. Hydrolysis reactions are influenced particularly by changes  
 2790 in concentration because water is one of the species in the equilibrium. For example, hydrolysis  
 2791 of the uranyl ion is represented by (Choppin et al., 1995, p.243):



2793 At tracer quantities, the equilibrium will shift to the left as the amount of the uranyl ion  
2794 decreases. At  $10^{-3}$  molar (pH 6), the uranyl ion is 50 percent polymerized; at  $10^{-6}$  molar, there is  
2795 negligible polymerization.

2796 Interactions of radionuclides with impurities present special problems at low concentration.  
2797 Difficulties include adsorption onto impurities such as dust, silica, or colloidal or suspended  
2798 material, or adsorption onto the walls of the container. Generally,  $10^{-8}$  to  $10^{-7}$  moles are needed to  
2799 cover a container's walls; but at tracer concentrations, much less is present (Choppin et al., 1995,  
2800 p. 242). Adsorption depends on (see *Surface Adsorption* within Section 14.8.4.1, "Coprecipita-  
2801 tion Processes"):

2802 • *Concentration*. A larger percentage is adsorbed at lower tracer concentrations than at higher  
2803 concentrations, because a larger surface area is available compared to the amount of tracer  
2804 present. Dilution with carrier decreases the amount of tracer adsorbed because the carrier is  
2805 competing for adsorption, and the relative amount of tracer interacting with the walls is much  
2806 less.

2807 • *Chemical State*. Adsorption increases with charge on the ion.

2808 • *Nature of the Surface Material*. Surfaces that have a negative charge or that contain hydroxyl  
2809 groups can interact with cations through electrostatic attraction and hydrogen bonding,  
2810 respectively.

2811 • *pH*. Generally, adsorption decreases with a lower pH (higher hydrogen ion concentration)  
2812 because the ions interact with negatively-charged surfaces, and hydrogen bonding decreases  
2813 their ability to interact with metal ions.

2814 All these processes will reduce the quantity of analyte available for radiochemical procedures  
2815 and, therefore, the yield of a procedure. The amount measured by the detection process will be  
2816 correspondingly lower, introducing additional error and uncertainty that would go undetected at  
2817 normal concentrations.

2818 Adsorption can be useful, however. For example, carrier-free yttrium ( $Y^{+3}$ ) is quantitatively  
2819 adsorbed onto filter paper from basic strontium solutions at concentrations at which yttrium  
2820 hydroxide,  $Y(OH)_3$ , will not precipitate. Also, carrier-free niobium (Nb) has been adsorbed on  
2821 glass fiber filters for a fast specific separation technique (Friedlander et al., 1981, p. 296).

2822 Specific behavior characteristics of compounds in separation techniques are further described  
2823 below. Additional discussion can also be found in the respective sections found earlier in this  
2824 document that describe each separation technique.

#### 2825 14.9.3.2 Coprecipitation

2826 Often, the concentration of tracer is so low that precipitation will not occur in the presence of a  
2827 counter-ion that, at normal concentrations, would produce an insoluble salt. Under these  
2828 conditions, carriers are used to coprecipitate the tracer. (Coprecipitation is described in  
2829 Section 14.8)

#### 2830 14.9.3.3 Deposition on Nonmetallic Solids

2831 Radionuclides can be deposited onto preformed ionic solids, charcoal, and ion-exchange resins  
2832 (Wahl and Bonner, 1951, p. 124). The mechanisms of adsorption onto preformed ionic solids are  
2833 similar to those responsible for coprecipitation: counter-ion exchange and isomorphous exchange  
2834 (Section 14.8, "Precipitation and Coprecipitation"). Adsorption is favored by a large surface area,  
2835 charge of the solid and radionuclide, solubility of compound formed between the solid and the  
2836 radionuclide, and time of contact; however, it depends, to a large extent, on whether or not the  
2837 radionuclide ion can fit into the crystal lattice of the precipitate. Similarly, adsorption onto  
2838 charcoal depends on the amount of charcoal and its surface area, time of contact, and nature of  
2839 the surface, because it can be modified by the presence of other ions or molecules.

2840 Adsorption of radionuclides, with and without carriers (Friedlander et al., 1981, p. 297), onto  
2841 ion-exchange resins, followed by selective elution, has been developed into a very efficient  
2842 separation technique (Wahl and Bonner, 1951, p. 145) (see Section 14.6.4, "Ion-Exchange  
2843 Chromatography"). Friedlander et al. (1981), illustrates this phenomenon:

2844 "Ion-exchange separations generally work as well with carrier-free tracers as with weighable  
2845 amounts of ionic species. A remarkable example was the original isolation of mendelevium at  
2846 the level of a few atoms (p. 298)...The transuranium elements in the solution were ...  
2847 separated from one another by elution ...through a cation-exchange column" (p. 450).

#### 2848 14.9.3.4 Radiocolloid Formation

2849 At the tracer level, a radionuclide solution is not necessarily truly homogeneous, but can be a  
2850 microparticle (colloid) of variable size or aggregation (Adolff and Guillaumont, 1993, p. 196).  
2851 Carrier-free tracers can become colloidal by two mechanisms:

## *Separation Techniques*

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2852 1. Sorption onto a preexisting colloidal impurity (approximately 0.001  $\mu$  to 0.5  $\mu$ ), such as  
2853 dust, cellulose fibers, glass fragments, organic material, and polymeric metal hydrolysis  
2854 products (Choppin et al., 1995, p. 243; Adolff and Guillaumont, 1993, p. 196)

2855 2. Polycondensation of a monomeric species consisting of aggregates of  $10^3$  to  $10^7$   
2856 radioactive atoms (Adolff and Guillaumont, 1993, p. 197)

2857 The presence of radiocolloids in solution can be detected by one or more of the following  
2858 characteristics of the solution, which is not typical behavior of a true solution (Adolff and  
2859 Guillaumont, 1993, p. 196):

2860 • The radionuclide can be separated from solution by a physical method such as ultrafiltration  
2861 or ultracentrifugation.

2862 • The radionuclide does not follow the laws of a true solution when a chemical gradient  
2863 (diffusion, dialysis, isotopic exchange) or electrical gradient (electrophoresis, electrolysis,  
2864 electro dialysis) is applied.

2865 • Adsorption on solid surfaces and spontaneous deposition differ from those effects observed  
2866 for radionuclides in true solution.

2867 • Autoradiography reveals the formation of aggregates of radioactive atoms.

2868 Several factors affect the formation of radiocolloids (Wahl and Bonner, 1951, pp. 145-148):

2869 • *Solubility of the Tracer.* The tendency of the tracer radionuclide to hydrolyze and form an  
2870 insoluble species with another component of the solution favors radiocolloid formation,  
2871 while the presence of ligands that form soluble complexes hinders formation; low pH tends  
2872 to minimize hydrolysis of metallic radionuclides.

2873 • *Foreign Particles.* The presence of foreign particles provides sites for the tracer to adsorb  
2874 onto their surfaces; solutions containing ultrapure water prepared with micropore filters  
2875 reduce their presence, although the preparation of water completely free of suspended  
2876 particles is difficult.

2877 • *Electrolytes.* Electrolytes affect the nature (species) of the tracer ions in solution (see Section  
2878 14.10, *Radiochemical Equilibrium*), as well as the charge on both the radiocolloid and the  
2879 foreign particle from which the colloid might have been derived.

2880 • *Solvent.* Polar and nonpolar solvents can favor the formation of radiocolloids, depending on  
2881 the specific radiocolloid itself.

2882 • *Time.* The amount of radiocolloidal formation generally increases with the age of solution.

#### 2883 14.9.3.5 Distribution (Partition) Behavior

2884 Distribution (partition) coefficients, which reflect the behavior of solutes during solvent  
2885 extraction procedures (Section 14.4, “Solvent Extraction”), are virtually independent of  
2886 concentration down to tracer concentrations (Friedlander et al., 1981, p. 299). Whenever the  
2887 radioactive substance itself changes into a different form, however, the coefficient naturally  
2888 changes, affecting the distribution between phases during extraction or any distribution  
2889 phenomena, such as ion-exchange or gas-liquid chromatography (Section 14.7, “Chromatog-  
2890 raphy”). Several properties of tracer solutions can alter the physical or chemical form of the  
2891 radionuclide in solution and alter its distribution behavior (Wahl and Bonner, 1951, pp. 149-  
2892 151):

2893 • Radiocolloid formation might concentrate the radionuclide in the alternate phase or at the  
2894 interface between the phases.

2895 • Shift in equilibrium during complex-ion formation or hydrolysis reactions can alter the  
2896 concentration of multiple radionuclide species in solution (Section 14.9.3.1, “Characteristics  
2897 of Tracers”).

#### 2898 14.9.3.6 Vaporization

2899 Radioisotope concentrations that challenge the minimum detectible concentration (MDC) can be  
2900 vaporized from solid surfaces or solution (Section 14.5, “Volatilization and Distillation”). Most  
2901 volatilization methods of these trace quantities of radionuclides can be performed without  
2902 specific carriers, but some nonisotopic carrier gas might be required (Friedlander et al., 1981,  
2903 p. 300).

2904 Vaporization of these amounts of materials from solid surfaces differs from the usual process of  
2905 vaporization of macroamounts of material, because the surface of the solid is usually not  
2906 completely covered with the radionuclide (Wahl and Bonner, 1951, pp. 151-158). Carrier-free  
2907 radionuclides at the surface are bonded with the surface particles instead of with themselves, and  
2908 the bonds broken during the process are between the solid and the radioisotope, rather than

2909 between the radioisotope particles themselves. Additionally, the nature of the radioisotope can be  
2910 altered by small trace quantities of gases such as oxygen and water present in the vacuum.  
2911 Therefore, the identity of the radionuclide species vaporizing might be uncertain, and the data  
2912 from the procedure can be hard to interpret. The rate of vaporization of radioisotopes also  
2913 decreases with time, because the number of radioisotope particles available on the solid surface  
2914 decreases with time.

2915 Radioisotopes near the MDC and macroquantities of radionuclide solutes should behave very  
2916 similarly in vaporization experiments from solution, however, because both are present as a  
2917 small fraction of the solution. They are, therefore, surrounded and bonded to solvent molecules  
2918 rather than to other solute particles (Wahl and Bonner, 1951, p. 156). The nature of the solvent,  
2919 the pH, and the presence of electrolytes generally affect the solubility of the solute and its  
2920 vaporization behavior.

#### 2921 14.9.3.7 Oxidation and Reduction

2922 Some radionuclides exist in only one oxidation state in solution, but others can exist in several  
2923 stable states (Tables 14.1 and 14.2). If multiple states are possible, it might be difficult to  
2924 ascertain in which state the radionuclide actually exists because the presence of trace amounts of  
2925 oxidation or reduction (redox) impurities might convert the radionuclide to a state other than the  
2926 one in which it was prepared (Wahl and Bonner, 1951, pp. 158-159). Excess redox reagents can  
2927 often be added to the solution to convert the forms to a fixed ratio and keep the ratio constant  
2928 during subsequent procedures.

2929 For a redox equilibrium such as:



2931 the Nernst equation is used to calculate the redox potential, E, from the standard potential, E<sup>0</sup>:

$$2932 E = E^0 - kT \ln([\text{Pu}^{+4}][\text{Hg}^{+2}]/[\text{PuO}_2^{+2}][\text{H}^{+1}]^4)$$

2933 where k is a constant for the reaction (R/2F, containing the ideal gas constant, R, and Faraday's  
2934 constant, F) and T is the absolute temperature. Water and metallic mercury (Hg) do not appear in  
2935 the equation, because their activity is one for a pure substance. Minute concentrations of ions in  
2936 solution exhibit the same redox potential as macroquantities of ions because, E depends on the  
2937 ratio of ion concentrations and not their total concentration.

2938 Electrolysis of some solutions is used for electrodeposition of a carrier-free metal on an electrode  
2939 (Choppin et al., 1995, p. 246) or other substance, leaving the impurities in solution (Friedlander  
2940 et al., 1981, p. 301). The selectivity and efficiency, characteristic of deposition of macro-  
2941 quantities of ions at a controlled potential, is not observed, however, for these metals. The  
2942 activity of the ion is not known, even if the concentration is, because the activity coefficient is  
2943 dependent on the behavior of the mixed electrolytic system. In addition, the concentration of the  
2944 metal in solution might not be known because losses may occur through adsorption or  
2945 complexation with impurities. Electrolytic deposits are usually extremely thin—a property that  
2946 makes them useful for counting measurements (Wahl and Bonner, 1951, p. 162).

2947 Deposition by chemical displacement is sometimes used for the separation of tracer from bulk  
2948 impurities (Friedlander et al., 1981, p. 301). Polonium and lead spontaneously deposit from a  
2949 solution of hydrochloric acid onto a nickel disk at 85 °C (Blanchard, 1966). Alpha and beta  
2950 counting is then used to determine  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ . The same technique is frequently used in low-  
2951 level analysis of transuranic elements to remove lead and polonium so that they do not interfere  
2952 with the subsequent alpha analysis of the elements. Wahl and Bonner (1951, pp. 460-465)  
2953 contains a helpful table (6F) of electrochemical methods used for the oxidation and reduction of  
2954 carrier-free tracers.

## 2955 **14.10 Radiochemical Equilibrium**

### 2956 **14.10.1 Basic Principles of Equilibrium**

2957 Radiochemical analysis is based on the assumption that an element reacts the same chemically,  
2958 whether or not it is radioactive. This assumption is valid when the element (analyte) and the  
2959 carrier/tracer are in the same oxidation state, complex, or compound. The atomic weight of most  
2960 elements is great enough that the difference in atomic weight between the radionuclide of interest  
2961 and the carrier or tracer will not result in any chemical separation of the isotopes. This  
2962 assumption might not be valid for the very lightest elements (e.g., H, Li, Be, and B) when mass  
2963 fractionation or measuring techniques are used.

2964 Most radiochemical procedures involve the addition of one of the following:

- 2965 • A carrier of natural isotopic composition (i.e., the addition of stable strontium carrier to  
2966 determine  $^{89}\text{Sr}/^{90}\text{Sr}$ ; EPA, 1980, Method 905.0).
- 2967 • A stable isotope tracer (i.e., enriched  $^{18}\text{O}$ ,  $^{15}\text{N}$ , and  $^{14}\text{C}$ , are frequently used in mass  
2968 spectroscopy studies).

2969 • A radionuclide tracer (i.e., the addition of a known quantity of  $^{236}\text{Pu}$  tracer to determine  $^{239}\text{Pu}$   
2970 by alpha spectroscopy; DOE, 1990 and 1997, Method Pu-02).

2971 To achieve quantitative yields, there must be complete equilibration (isotopic exchange) between  
2972 the added isotope and all the analyte species present. In the first example, isotopic exchange of  
2973 the carrier with the radiostrontium is achieved and a weighable, stoichiometric compound of the  
2974 carrier and radionuclide are produced. The chemical recovery from the separation technique is  
2975 determined gravimetrically. Alternatively, a known quantity of an isocesiumtope is used and  
2976 determined independently by mass analysis, pulse-height analysis, or another counting technique.

2977 Carriers and tracers are added as soon in the sample preparation process as possible, usually after  
2978 the bulk sample is dried and homogenized, but before sample decomposition to ensure that the  
2979 chemistry of the carriers or tracers is truly representative of the radioisotope of interest. Thus,  
2980 losses occurring during sample preparation steps, before decomposition, are not quantified and  
2981 might not be detected, although losses during these earlier steps are usually minimized. Having  
2982 the carriers and tracers present during the sample decomposition provides an opportunity to  
2983 equilibrate the carrier or tracer with the sample so that the carrier, tracer, and analyte are in the  
2984 identical chemical form. While this can initially appear to be rather easy, in some cases it is  
2985 extremely difficult. The presence of multiple valence states and the formation of chemical  
2986 complexes are two conditions that introduce a host of equilibration problems (Section 14.2.2,  
2987 “Oxidation-Reduction Reactions”; Section 14.2.3, “Common Oxidation States”; and Section  
2988 14.2.4, “Oxidation State in Solution”). Crouthamel and Heinrich (1971, pp. 5473-5474) has an  
2989 excellent discussion of the intricacies and challenges associated with attaining true isotopic  
2990 exchange:

2991 “Fortunately, there are many reactions which have high exchange rates. This applies even  
2992 to many heterogeneous systems, as in the heterogeneous catalysis of certain electron  
2993 transfer reactions. In 1920, Hevesy, using ThB ( $^{212}\text{Pb}$ ), demonstrated the rapid exchange  
2994 between active lead nitrate and inactive lead chloride by the recrystallization of lead  
2995 chloride from the homogeneously mixed salts. The ionization of these salts leads to the  
2996 chemically identical lead ions, and a rapid isotopic exchange is expected. Similar  
2997 reversible reactions account for the majority of the rapid exchange reactions observed at  
2998 ordinary temperatures. Whenever possible, the analyst should conduct the isotope  
2999 exchange reaction through a known reversible reaction in a homogeneous system. The  
3000 true homogeneity of a system is not always obvious, particularly when dealing with the  
3001 very low concentrations of the carrier-free isotopes. Even the usually well-behaved alkali-  
3002 metal ions in carrier-free solutions will adsorb on the surfaces of their containment

3003 vessels or on colloidal and insoluble material in the solution. This is true especially in the  
3004 heavier alkali metals, rubidium and cesium. Cesium ions in aqueous solution have been  
3005 observed to absorb appreciably to the walls of glass vessels when the concentrations were  
3006 below  $10^{-6}$  g/mL.”

3007 The reaction described above can be written as follows:



3009 Any of the following techniques may be employed to achieve both chemical and isotopic  
3010 equilibration:

- 3011 • Careful adding, mixing, stirring, shaking, etc., to assure a homogeneous solution and prevent  
3012 layering.
- 3013 • Introducing the carrier or tracer in several different chemical forms or oxidation states,  
3014 followed by oxidation or reduction to a single state.
- 3015 • Treating the carrier or tracer and sample initially with strong oxidizing or reducing agents  
3016 during decomposition (e.g., wet ashing or fusion).
- 3017 • Carrying out repeated series of oxidation-reduction reactions.
- 3018 • Requiring that, at some point during the sample decomposition, all the species be together in  
3019 a clear solution.

3020 Once a true equilibration between carrier or tracer and sample occurs, the radiochemistry  
3021 problem shifts from one of equilibration to that of separation from other elements, and ultimately  
3022 a good recovery of the radionuclide of interest.

3023 Crouthamel and Heinrich summarizes the introduction to equilibration (isotopic exchange)  
3024 (Crouthamel and Heinrich, 1971, pp. 5475-5476):

3025 “Probably the best way to give the reader a feeling for the ways in which isotopic  
3026 exchange is achieved in practice is to note some specific examples from radiochemical  
3027 procedures. The elements which show strong tendencies to form radiocolloids in many  
3028 instances may be stabilized almost quantitatively as a particular complex species and  
3029 exchange effected. Zirconium, for example, is usually exchanged in strong nitric acid-

3030 hydrofluoric acid solution. In this medium, virtually all the zirconium forms a  $ZrF_6^{2-}$   
3031 complex. Niobium exchange is usually made in an oxalate or fluoride acid medium. The  
3032 exchange of ruthenium is accomplished through its maximum oxidation state, Ru(VIII)  
3033 which can be stabilized in a homogeneous solution and distilled as  $RuO_4$ . Exchange may  
3034 also be achieved by cycling the carrier through oxidation and reduction steps in the  
3035 presence of the radioactive isotope. An iodine carrier with possible valence states of -1 to  
3036 +7 is usually cycled through its full oxidation-reduction range to ensure complete  
3037 exchange. In a large number of cases, isotopic exchange is not a difficult problem;  
3038 however, the analyst cannot afford to relax his attention to this important step. He must  
3039 consider in each analysis the possibility of both the slow exchange of certain chemical  
3040 species in homogenous solution and the possible very slow exchange in heterogeneous  
3041 systems. In the latter case, this may consist simply of examining the solutions for  
3042 insoluble matter and taking the necessary steps to either dissolve or filter it and to assay  
3043 for possible radioactive content.”

3044 Also see the discussion of equilibration of specific radionuclides in Section 14.10.9, “Review of  
3045 Specific Radionuclides.”

#### 3046 **14.10.2 Oxidation State**

3047 Some radionuclides exist in solution in one oxidation state that does not change, regardless of the  
3048 kind of chemical treatment used for analysis. Cesium (Cs), radium, strontium, tritium ( $^3H$ ), and  
3049 thorium are in the +1, +2, +2, +1, and +4 oxidation states, respectively, during all phases of  
3050 chemical treatment. However, several radionuclides can exist in more than one state, and some  
3051 are notable for their tendency to exist in multiple states simultaneously, depending on the other  
3052 components present in the mixture. Among the former are cobalt, iron, iodine, and technetium,  
3053 and among the latter are americium, plutonium, and uranium. To ensure identical chemical  
3054 behavior during the analytical procedure, the radionuclide of interest and its carriers and/or  
3055 tracers in solution must be converted to identical oxidation states. The sample mixture containing  
3056 the carriers and/or tracer is treated with redox agents to convert each state initially present to the  
3057 same state, or to a mixture with the same ratio of states. Table 6E in Wahl and Bonner (1951, pp.  
3058 450-459) provides a list of traditional agents for the oxidation and reduction of carrier-free  
3059 tracers that is a useful first guide to the selection of conditions for these radioequilibrium  
3060 processes.

3061 **14.10.3 Hydrolysis**

3062 All metal ions (cations) in aqueous solution interact extensively with water, and, to a greater or  
3063 lesser extent, they exist as solvated cations (Katz et al., 1986, p. 1141):



3065 The more charged the cation, the greater is its interaction with water. Solvated cations, especially  
3066 those with +4, +3, and small +2 ions, tend to act as acids by hydrolyzing in solution. Simply  
3067 stated, *hydrolysis* is complexation where the ligand is the hydroxyl ion. To some extent, all metal  
3068 cations in solution undergo hydrolysis and exist as hydrated species. The hydrolysis reaction for a  
3069 metal ion is represented simply as (Choppin et al., 1995, p.650):



3071 Hydrolysis of the ferric ion ( $\text{Fe}^{+3}$ ) is a classical example:



3073 Considering the hydrated form of the cation, hydrolysis is represented by:



3075 In the latter equation, the hydrated complex ion associated with the hydroxide ion, is known as  
3076 the *aquo-hydroxo* species (Birkett et al., 1988, p. 2.7-3). As each equation indicates, hydrolysis  
3077 increases the acidity of the solution, and the concentration of the hydrogen ion (pH) affects the  
3078 position of equilibrium. An increase in acidity (increase in  $\text{H}^{+1}$  concentration; decrease in pH)  
3079 shifts the position of equilibrium to the left, decreasing hydrolysis, while a decrease in acidity  
3080 shifts it to the right, increasing hydrolysis. The extent of hydrolysis, therefore, depends on the pH  
3081 of the solution containing the radionuclide. The extent of hydrolysis is also influenced by the  
3082 radius and charge of the cation (charge/radius ratio). Generally, a high ratio increases the  
3083 tendency of a cation to hydrolyze. A ratio that promotes hydrolysis is generally found in small  
3084 cations with a charge greater than one ( $\text{Be}^{+2}$ , for example). The thorium cation,  $\text{Th}^{+4}$ , with a  
3085 radius three times the size of the beryllium ion but a +4 charge, is hydrolyzed extensively, even at  
3086 a pH of four (Baes and Mesmer, 1976, p. 158). It is not surprising, therefore, that hydrolysis is an  
3087 especially important factor in the behavior of several metallic radionuclides in solution, and is  
3088 observed in the transition, lanthanide, and actinide groups. For the actinide series, the +4 cations  
3089 have the greatest charge/radius ratio and undergo hydrolysis most readily. Below pH 3, the

3090 hydrolysis of  $\text{Th}^{4+}$  is negligible, but at higher pH, extensive hydrolysis occurs. Uranium(IV)  
3091 undergoes hydrolysis in solution at a pH above 2.9 with  $\text{U}(\text{OH})_3^+$  being the predominant  
3092 hydrolyzed species. Neptunium ions undergo hydrolysis in dilute acid conditions with evidence  
3093 of polymer formation in acidic solutions less than 0.3 M. The hydrolysis of plutonium is the most  
3094 severe, often leading to polymerization (see Section 14.10.4, "Polymerization"). In summary, the  
3095 overall tendency of actinides to hydrolyze decreases in the order (Katz et al., 1986, p. 1145):



3097 where "An" represents the general chemical symbol for an actinide.

3098 For some cations, hydrolysis continues past the first reaction with water, increasing the number  
3099 of hydroxide ions ( $\text{OH}^{-1}$ ) associated with the cation in the aquo-hydroxo species:



3102 This process can, in some cases, conclude with the precipitation of an insoluble hydroxide, such  
3103 as ferric hydroxide. "Soluble hydrolysis products are especially important in systems where the  
3104 cation concentrations are relatively low, and hence the range of pH relatively wide over which  
3105 such species can be present and can profoundly affect the chemical behavior of the metal" (Baes  
3106 and Mesmer, 1976, p. 3).

3107 Solutions containing trace concentrations of metallic radionuclides qualify as an example of  
3108 these systems. The form of hydrolysis products present can control important aspects of chemical  
3109 behavior such as (Baes and Mesmer, 1976, p. 3):

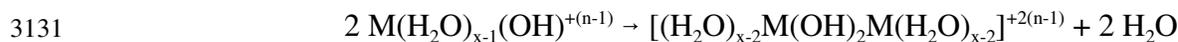
- 3110
- 3111 • Adsorption of the radionuclide on surfaces, especially on mineral and soil particles.
  - 3112 • Tendency to coagulate colloidal particles.
  - 3113 • Solubility of the hydroxide or metal oxide.
  - 3114 • Extent of complex formation in solution.
  - 3115 • Extent of extraction from solution by various reagents.
  - Ability to oxidize or reduce the radionuclide to another oxidation state.

3116 Thus, a knowledge of the identity and stability of radionuclide ion hydrolysis products is  
3117 important in understanding or predicting the chemical behavior of trace quantities of  
3118 radionuclides in solution (Baes and Mesmer, 1976, p. 3). As the equilibrium equation indicates,

3119 H<sup>+</sup> is produced as cations hydrolyze. Undesirable consequences of hydrolysis can, therefore, be  
3120 minimized or eliminated by the addition of acid to the analytical mixture to reverse hydrolysis or  
3121 prevent it from occurring. Numerous steps in radioanalytical procedures are performed at low pH  
3122 to eliminate hydrolytic effects. It is also important to know the major and minor constituents of  
3123 any sample, since hydrolysis effects are a function of pH and metal concentration. Thus,  
3124 maintaining the pH of a high iron-content soil sample below pH 3.0 is important, even if iron is  
3125 not the analyte.

#### 3126 **14.10.4 Polymerization**

3127 The hydrolysis products of radionuclide cations described in the preceding section are  
3128 monomeric—containing only one metal ion. Some of these monomers can spontaneously form  
3129 polymeric metal hydroxo polymers in solution, represented by formation of the dimer (Birkett  
3130 et al., 1988, p. 2.8-1):



3132 The polymers contain -OH-bridges between the metal ions that, under high temperature,  
3133 prolonged aging, and/or high pH, can convert to -O-bridges, leading eventually to precipitation of  
3134 hydrated metal oxides. Birkett et al. (1988) states that:

3135 “Formation of polymeric hydroxo species has been reported for most metals, although in  
3136 some cases, the predominant species in solution is the monomer. Some metals form only  
3137 dimers or trimers, while a few form much larger, higher-molecular-weight polymeric species.

3138 “Increasing the pH of a metal ion solution, by shifting the position of hydrolysis  
3139 equilibrium ..., results in an increased concentration of hydrolyzed species ..., which in turn  
3140 causes increased formation of polymeric species ... . Diluting a solution has two opposing  
3141 effects on the formation of polymeric species:

3142 “(1) Because dilution of acidic solutions causes a decrease in H<sup>+</sup> concentration (i.e.,  
3143 an increase in pH), it causes a shift in the hydrolyzed equilibrium toward  
3144 formation of hydrolyzed species.

3145 “(2) On the other hand, dilution decreases the ratio of polymeric to monomeric  
3146 complexes in solution. For metals that form both monomeric and polymeric  
3147 complexes, this means that monomeric species predominate beyond a certain level  
3148 of dilution” (Birkett et al., 1988, p. 2.8-2).

3149 Because this type of polymerization begins with hydrolysis of a cation, minimizing or  
3150 eliminating polymerization can be achieved by the addition of acid to lower the pH of the  
3151 analytical solution to prevent hydrolysis (Section 14.10.3, “Hydrolysis”).

#### 3152 **14.10.5 Complexation**

3153 Radionuclides exist as metal ions in solution, and many have a tendency to form stable complex  
3154 ions with molecules or anions present as analytical reagents or impurities. The tendency to form  
3155 complex ions is, to a considerable extent, an expression of the same properties that lead to  
3156 hydrolysis; high positive charge on a +3 or +4 ion provides a strong driving force for the  
3157 interaction with ligands (Katz et al., 1986, p. 1146) (Section 14.3, “Complexation”).

3158 Complex-ion formation by a radionuclide alters its form, introducing in solution additional  
3159 species of the radionuclide whose concentrations depend on the magnitude of the formation  
3160 constant(s). Alternate forms have different physical and chemical properties, and behave  
3161 differently in separation techniques, such as extraction or partition chromatography. The behavior  
3162 of alternate forms of radionuclides can present problems in the separation scheme that should be  
3163 avoided if possible or addressed in the protocol. Some separation schemes, however, take  
3164 advantage of the behavior of alternate radionuclide species formed by complexation, which can  
3165 alter the solubility of the radionuclides in a solvent or their bonding to an ion-exchange resin  
3166 (Section 14.3.4.2, “Separation by Solvent Extraction and Ion-Exchange Chromatography”).

#### 3167 **14.10.6 Radiocolloid Interference**

3168 The tendency of some radionuclides in solution, particularly tracer levels of radionuclides, to  
3169 form radiocolloids, alters the physical and chemical behavior of those radionuclides (see Section  
3170 14.9.3.4, “Radiocolloid Formation”). Radioanalytical separations will not perform as expected in  
3171 solutions containing radiocolloids, particularly as the solubility of the radionuclide species  
3172 decreases.

3173 Solutions containing large molecules, such as polymeric metal hydrolysis products, are more  
3174 likely to form radiocolloids (Choppin et al., 1995, p. 243). “If the solution is kept at sufficiently  
3175 low pH and extremely free of foreign particles, sorption and radiocolloid formation are usually  
3176 avoided as major problems” (Choppin et al. 1995, p. 243). If tracer levels of radionuclides are  
3177 present, trace impurities become especially significant in the radiochemical procedure, and  
3178 should be minimized or avoided whenever possible (Crouthamel and Heinrich, 1971, p. 5493).

3179 Crouthamel and Heinrich provide some specific insight into radiocolloidal interference in the  
3180 equilibration problem:

3181 “The transition metals tend to form radiocolloids in solution, and in these heterogeneous  
3182 systems the isotopic exchange reaction between a radiocolloid and inactive carrier added to  
3183 the solution is sometimes slow and, more often, incomplete. Elements which show a strong  
3184 tendency to form radiocolloids, even in macro concentrations and acid solutions, are titanium,  
3185 zirconium, hafnium, niobium, tantalum, thorium, and protactinium, and, to a lesser degree,  
3186 the rare earths. Other metals also may form radiocolloids, but generally offer a wider choice  
3187 of valence states which may be stabilized in aqueous solutions” (Crouthamel and Heinrich,  
3188 1971, p. 5474).

3189 **14.10.7 Isotope Dilution Analysis**

3190 The basic concept of *isotope dilution analysis* is to measure the changes in specific activity of a  
3191 substance upon its incorporation into a system containing an unknown amount of that substance.  
3192 Friedlander et al. (1981), define *specific activity*:

3193 “Specific activity is defined as the ratio of the number of radioactive atoms to the total  
3194 number of atoms of a given element in the sample ( $N^*/N$ ). In many cases where only the  
3195 ratios of specific activities are needed, quantities proportional to  $N^*/N$ , such as activity/mole,  
3196 are referred to as specific activity” (Friedlander et al., 1981, p. 432).

3197 For example, isotope dilution can be used to determine the amount of some inactive material A  
3198 in a system (Wang et al., 1975). To the system containing x grams of an unknown weight of the  
3199 inactive form of A, y grams of active material A\* of known activity D is added. The specific  
3200 activity of the added active material,  $S_1$ , is given by:

3201 
$$S_1 = D/y$$

3202 After ensuring isotopic exchange, the mixture of A and A\* is isolated, but not necessarily  
3203 quantitatively, and purified. The specific activity,  $S_2$ , is measured. Owing to the conservation of  
3204 matter,

3205 
$$S_2 = D/(x + y)$$

3206 and by substituting for  $S_1 y$  for D and rearranging, the amount x of inactive A is given as

3207  $x = y(S_1/S_2 - 1)$

3208 However, this equation is valid only if complete isotopic exchange has occurred, a task not  
3209 always easy to achieve.

#### 3210 **14.10.8 Masking and Demasking**

3211 Masking is the prevention of reactions that are normally expected to occur through the presence  
3212 or addition of a masking reagent. Masking reactions can be represented by the general reversible  
3213 equation:



3215 where A is the normal reacting molecule or ion, and Ms is the masking agent. The decreased  
3216 concentration of A at equilibrium determines the efficiency of masking. An excess of masking  
3217 agent favors the completeness of masking, as expected from LeChatelier's Principle. Feigl (1936,  
3218 p. 409) has described *masking reagent* and the *masking* of a reaction as follows: "... the  
3219 concentration of a given ion in a solution can be so diminished by the addition of substances  
3220 which unite with the ion to form complex salts that an ion product sufficient to form a precipitate  
3221 or cause a color reaction is no longer obtained. Thus we speak of the *masking* of a reaction and  
3222 call the reagent responsible for the disappearance of the ions necessary for the reaction, the  
3223 *masking reagent*." The concepts of masking and demasking are discussed further in Perrin (1979,  
3224 pp. 600-643) and in Dean (1995, pp. 2.9-2.15).

3225 Masking techniques are frequently used in analytical chemistry because they often provide  
3226 convenient and efficient methods to avoid the effects of unwanted components of a system  
3227 without having to separate the interferant physically. Therefore, the selectivity of many analytical  
3228 techniques can be increased through masking techniques. For example, copper can be prohibited  
3229 from carrying on ferric hydroxide at pH 7 by the addition of ammonium ions to complex the  
3230 copper ions. Fe<sup>3+</sup> and Al<sup>3+</sup> both interfere with the extraction of the +3 actinides and lanthanides in  
3231 some systems, but Fe<sup>3+</sup> can be easily masked through reduction with ascorbic acid, and Al<sup>3+</sup> can  
3232 be masked through complexation with fluoride ion (Horwitz et al., 1993 and 1994). In another  
3233 example, uranium can be isolated on a U/TEVA column (Eichrom Industries, Inc., Darien, IL)  
3234 from nitric acid solutions by masking the tetravalent actinides with oxalic acid; the tetravalent  
3235 actinides are complexed and pass through the column, whereas uranium is extracted (SpecNews,  
3236 1993). Strontium and barium can be isolated from other metals by cation exchange from a  
3237 solution of water, pyridine, acetic acid and glycolic acid. The other metals form neutral or  
3238 negative complexes and pass through the cation column, while strontium and barium are retained

3239 (Orlandini, 1972). Masking phenomena are present in natural systems as well. It has been  
 3240 demonstrated that humic and fulvic acids can complex heavy metals such that they are no longer  
 3241 bioavailable and are, therefore, not taken up by plants. Tables 14.17 and 14.18 list common  
 3242 masking agents.

3243 **TABLE 14.17 — Masking agents for ions of various metals** <sup>(1)</sup>

Metal	Masking Agent
Ag	Br <sup>-</sup> , citrate, Cl <sup>-</sup> , CN <sup>-</sup> , I <sup>-</sup> , NH <sub>3</sub> , SCN <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>-2</sup> , thiourea, thioglycolic acid, diethyldithiocarbamate, thiosemicarbazide, bis(2-hydroxyethyl)dithiocarbamate
Al	Acetate, acetylacetone, BF <sub>4</sub> <sup>-</sup> , citrate, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , EDTA, F <sup>-</sup> , formate, 8-hydroxyquinoline-5-sulfonic acid, mannitol, 2,3-mercaptopropanol, OH <sup>-</sup> , salicylate, sulfosalicylate, tartrate, triethanolamine, tiron
As	Citrate, 2,3-dimercaptopropanol, NH <sub>2</sub> OH·HCl, OH <sup>-</sup> , S <sub>2</sub> <sup>-2</sup> , tartrate
Au	Br <sup>-</sup> , CN <sup>-</sup> , NH <sub>3</sub> , SCN <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>-2</sup> , thiourea
Ba	Citrate, cyclohexanediaminetetraacetic acid, <i>N,N</i> -dihydroxyethylglycine, EDTA, F <sup>-</sup> , SO <sub>4</sub> <sup>-2</sup> , tartrate
Be	Acetylacetone, citrate, EDTA, F <sup>-</sup> , sulfosalicylate, tartrate
Bi	Citrate, Cl <sup>-</sup> , 2,3-dimercaptopropanol, dithizone, EDTA, I <sup>-</sup> , OH <sup>-</sup> , Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> , SCN <sup>-</sup> , tartrate, thiosulfate, thiourea, triethanolamine
Ca	BF <sub>4</sub> <sup>-</sup> , citrate, <i>N,N</i> -dihydroxyethylglycine, EDTA, F <sup>-</sup> , polyphosphates, tartrate
Cd	Citrate, CN <sup>-</sup> , 2,3-dimercaptopropanol, dimercaptosuccinic acid, dithizone, EDTA, glycine, I <sup>-</sup> , malonate, NH <sub>3</sub> , 1,10-phenanthroline, SCN <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>-2</sup> , tartrate
Ce	Citrate, <i>N,N</i> -dihydroxyethylglycine, EDTA, F <sup>-</sup> , PO <sub>4</sub> <sup>-3</sup> , reducing agents (ascorbic acid), tartrate, tiron
Co	Citrate, CN <sup>-</sup> , diethyldithiocarbamate, 2,3-dimercaptopropanol, dimethylglyoxime, ethylenediamine, EDTA, F <sup>-</sup> , glycine, H <sub>2</sub> O <sub>2</sub> , NH <sub>3</sub> , NO <sub>2</sub> <sup>-</sup> , 1,10-phenanthroline, Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> , SCN <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>-2</sup> , tartrate
Cr	Acetate, (reduction with) ascorbic acid + KI, citrate, <i>N,N</i> -dihydroxyethylglycine, EDTA, F <sup>-</sup> , formate, NaOH + H <sub>2</sub> O <sub>2</sub> , oxidation to CrO <sub>4</sub> <sup>-2</sup> , Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> , sulfosalicylate, tartrate, triethylamine, tiron
Cu	Ascorbic acid + KI, citrate, CN <sup>-</sup> , diethyldithiocarbamate, 2,3-dimercaptopropanol, ethylenediamine, EDTA, glycine, hexacyanocobalt(III)(3-), hydrazine, I <sup>-</sup> , NaH <sub>2</sub> PO <sub>2</sub> , NH <sub>2</sub> OH·HCl, NH <sub>3</sub> , NO <sub>2</sub> <sup>-</sup> , 1,10-phenanthroline, S <sup>-2</sup> , SCN <sup>-</sup> + SO <sub>3</sub> <sup>-2</sup> , sulfosalicylate, tartrate, thioglycolic acid, thiosemicarbazide, thiocarbohydrazide, thiourea
Fe	Acetylacetone, (reduction with) ascorbic acid, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , citrate, CN <sup>-</sup> , 2,3-dimercaptopropanol, EDTA, F <sup>-</sup> , NH <sub>3</sub> , NH <sub>2</sub> OH·HCl, OH <sup>-</sup> , oxine, 1,10-phenanthroline, 2,2'-bipyridyl, PO <sub>4</sub> <sup>-3</sup> , P <sub>2</sub> O <sub>7</sub> <sup>-4</sup> , S <sup>-2</sup> , SCN <sup>-</sup> , SnCl <sub>2</sub> , S <sub>2</sub> O <sub>3</sub> <sup>-2</sup> , sulfamic acid, sulfosalicylate, tartrate, thioglycolic acid, thiourea, tiron, triethanolamine, trithiocarbonate
Ga	Citrate, Cl <sup>-</sup> , EDTA, OH <sup>-</sup> , oxalate, sulfosalicylate, tartrate
Ge	F <sup>-</sup> , oxalate, tartrate
Hf	See Zr
Hg	Acetone, (reduction with) ascorbic acid, citrate, Cl <sup>-</sup> , CN <sup>-</sup> , 2,3-dimercaptopropan-1-ol, EDTA, formate, I <sup>-</sup> , SCN <sup>-</sup> , SO <sub>3</sub> <sup>-2</sup> , tartrate, thiosemicarbazide, thiourea, triethanolamine
In	Cl <sup>-</sup> , EDTA, F <sup>-</sup> , SCN <sup>-</sup> , tartrate, thiourea, triethanolamine
Ir	Citrate, CN <sup>-</sup> , SCN <sup>-</sup> , tartrate, thiourea
La	Citrate, EDTA, F <sup>-</sup> , oxalate, tartrate, tiron

Separation Techniques

	Metal	Masking Agent
3266	Mg	Citrate, $C_2O_4^{2-}$ , cyclohexane-1,2-diaminetetraacetic acid, <i>N,N</i> -dihydroxyethylglycine, EDTA, F <sup>-</sup> , glycol, hexametaphosphate, OH <sup>-</sup> , $P_2O_7^{4-}$ , triethanolamine
3267	Mn	Citrate, CN <sup>-</sup> , $C_2O_4^{2-}$ , 2,3-dimercaptopropanol, EDTA, F <sup>-</sup> , $Na_5P_3O_{10}$ , oxidation to $MnO_4^-$ , $P_2O_7^{4-}$ , reduction to Mn(II) with $NH_2OH \cdot HCl$ or hydrazine, sulfosalicylate, tartrate, triethanolamine, triphosphate, tiron
3268	Mo	Acetylacetone, ascorbic acid, citrate, $C_2O_4^{2-}$ , EDTA, F <sup>-</sup> , $H_2O_2$ , hydrazine, mannitol, $Na_5P_3O_{10}$ , $NH_2OH \cdot HCl$ , oxidation to molybdate, SCN <sup>-</sup> , tartrate, tiron, triphosphate
3269	Nb	Citrate, $C_2O_4^{2-}$ , F <sup>-</sup> , $H_2O_2$ , OH <sup>-</sup> , tartrate
3270	Nd	EDTA
3271	$NH_4^+$	HCHO
3272	Ni	Citrate, CN <sup>-</sup> , <i>N,N</i> -dihydroxyethylglycine, dimethylglyoxime, EDTA, F <sup>-</sup> , glycine, malonate, $Na_5P_3O_{10}$ , $NH_3$ , 1,10-phenanthroline, SCN <sup>-</sup> , sulfosalicylate, thioglycolic acid, triethanolamine, tartrate
3273	Np	F <sup>-</sup>
3274	Os	CN <sup>-</sup> , SCN <sup>-</sup> , thiourea
3275	Pa	$H_2O_2$
3276	Pb	Acetate, $(C_6H_5)_4AsCl$ , citrate, 2,3-dimercaptopropanol, EDTA, I <sup>-</sup> , $Na_5P_3O_{10}$ , $SO_4^{2-}$ , $S_2O_3^{2-}$ , tartrate, tiron, tetraphenylarsonium chloride, triethanolamine, thioglycolic acid
3277	Pd	Acetylacetone, citrate, CN <sup>-</sup> , EDTA, I <sup>-</sup> , $NH_3$ , $NO_2^-$ , SCN <sup>-</sup> , $S_2O_3^{2-}$ , tartrate, triethanol-amine
3278	Pt	Citrate, CN <sup>-</sup> , EDTA, I <sup>-</sup> , $NH_3$ , $NO_2^-$ , SCN <sup>-</sup> , $S_2O_3^{2-}$ , tartrate, urea
3279	Pu	Reduction to Pu(IV) with sulfamic acid
3280	Rare	$C_2O_4^{2-}$ , citrate, EDTA, F <sup>-</sup> , tartrate Earths
3281	Re	Oxidation to perrhenate
3282	Rh	Citrate, tartrate, thiourea
3283	Ru	CN <sup>-</sup> , thiourea
3284	Sb	Citrate, 2,3-dimercaptopropanol, EDTA, I <sup>-</sup> , OH <sup>-</sup> , oxalate, $S^{2-}$ , $S_2^{2-}$ , $S_2O_3^{2-}$ , tartrate, triethanolamine
3285	Sc	Cyclohexane-1,2-diaminetetraacetic acid, F <sup>-</sup> , tartrate
3286	Se	Citrate, F <sup>-</sup> , I <sup>-</sup> , reducing agents, $S^{2-}$ , $SO_3^{2-}$ , tartrate
3287	Sn	Citrate, $C_2O_3^{2-}$ , 2,3-dimercaptopropanol, EDTA, F <sup>-</sup> , I <sup>-</sup> , OH <sup>-</sup> , oxidation with bromine water, $PO_4^{3-}$ , tartrate, triethanolamine, thioglycolic acid
3288	Ta	Citrate, F <sup>-</sup> , $H_2O_2$ , OH <sup>-</sup> , oxalate, tartrate
3289	Te	Citrate, F <sup>-</sup> , I <sup>-</sup> , reducing agents, $S^{2-}$ , sulfite, tartrate
3290	Th	Acetate, acetylacetone, citrate, EDTA, F <sup>-</sup> , $SO_4^{2-}$ , 4-sulfobenzeneearsonic acid, sulfosalicylic acid, tartrate, triethanolamine
3291	Ti	Ascorbic acid, citrate, F <sup>-</sup> , gluconate, $H_2O_2$ , mannitol, $Na_5P_3O_{10}$ , OH <sup>-</sup> , $SO_4^{2-}$ , sulfosalicylic acid, tartrate, triethanolamine, tiron
3292	Tl	Citrate, Cl <sup>-</sup> , CN <sup>-</sup> , EDTA, HCHO, hydrazine, $NH_2OH \cdot HCl$ , oxalate, tartrate, triethanolamine
3293	U	Citrate, $(NH_4)_2CO_3$ , $C_2O_4^{2-}$ , EDTA, F <sup>-</sup> , $H_2O_2$ , hydrazine + triethanolamine, $PO_4^{3-}$ , tartrate
3294	V	(reduction with) Ascorbic acid, hydrazine, or $NH_2OH \cdot HCl$ , CN <sup>-</sup> , EDTA, $H_2O_2$ , mannitol, oxidation to vanadate, triethanolamine, tiron

	<b>Metal Masking Agent</b>
3295	W Citrate, F <sup>-</sup> , H <sub>2</sub> O <sub>2</sub> , hydrazine, Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> , NH <sub>2</sub> OH·HCl, oxalate, SCN <sup>-</sup> , tartrate, tiron, triphosphate, oxidation to tungstate
3296	Y Cyclohexane-1,2-diaminetetraacetic acid, F <sup>-</sup>
3297	Zn Citrate, CN <sup>-</sup> , <i>N,N</i> -dihydroxyethylglycine, 2,3-dimercaptopropanol, dithizone, EDTA, F <sup>-</sup> , glycerol, glycol, hexacyanoferrate(II)(4-), Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> , NH <sub>3</sub> , OH <sup>-</sup> , SCN <sup>-</sup> , tartrate, triethanolamine
3298	Zr Arsenazo, carbonate, citrate, C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , cyclohexane-1,2-diaminetetraacetic acid, EDTA, F <sup>-</sup> , H <sub>2</sub> O <sub>2</sub> , PO <sub>4</sub> <sup>3-</sup> , P <sub>2</sub> O <sub>7</sub> <sup>4-</sup> , pyrogallol, quinalizarinesulfonic acid, salicylate, SO <sub>4</sub> <sup>2-</sup> + H <sub>2</sub> O <sub>2</sub> , sulfosalicylate, tartrate, triethanolamine
3299	(1) Compiled from Perrin (1979, pp. 609-611) and Dean (1995, pp. ?)

TABLE 14.18 — Masking agents for anions and neutral molecules

	<b>Anion or Neutral Molecule</b>	<b>Masking Agent</b>
3303	Boric Acid	F <sup>-</sup> , glycol, mannitol, tartrate, and other hydroxy acids
3304	Br <sup>-</sup>	Hg(II)
3305	Br <sub>2</sub>	Phenol, sulfosalicylic acid
3306	BrO <sub>3</sub> <sup>-</sup>	Reduction with arsenate(III), hydrazine, sulfite, or thiosulfate
3307	Chromate(VI)	Reduction with arsenate(III), ascorbic acid, hydrazine, hydroxylamine, sulfite, or thiosulfate
3308	Citrate	Ca(II)
3309	Cl <sup>-</sup>	Hg(II), Sb(III)
3310	Cl <sub>2</sub>	Sulfite
3311	ClO <sub>3</sub> <sup>-</sup>	Thiosulfate
3312	ClO <sub>4</sub> <sup>-</sup>	Hydrazine, sulfite
3313	CN <sup>-</sup>	HCHO, Hg(II), transition-metal ions
3314	EDTA	Cu(II)
3315	F <sup>-</sup>	Al (III), Be(II), boric acid, Fe(III), Th(IV), Ti(IV), Zr(IV)
3316	Fe(CN) <sub>3</sub> <sup>3-</sup>	Arsenate(III), ascorbic acid, hydrazine, hydroxylamine, thiosulfate
3317	Germanic Acid	Glucose, glycerol, mannitol
3318	I <sup>-</sup>	Hg(II)
3319	I <sub>2</sub>	Thiosulfate
3320	IO <sub>3</sub> <sup>-</sup>	Hydrazine, sulfite, thiosulfate
3321	IO <sub>4</sub> <sup>-</sup>	Arsenate(III), hydrazine, molybdate(VI), sulfite, thiosulfate
3322	MnO <sub>4</sub> <sup>-</sup>	Reduction with arsenate(III), ascorbic acid, azide, hydrazine, hydroxylamine, oxalic acid,
3323	MoO <sub>4</sub> <sup>2-</sup>	sulfite, or thiosulfate
3324	NO <sub>2</sub> <sup>-</sup>	Citrate, F <sup>-</sup> , H <sub>2</sub> O <sub>2</sub> , oxalate, thiocyanate + Sn(II)
3325	Oxalate	Co(II), sulfamic acid, sulfanilic acid, urea
3326	Phosphate	Molybdate(VI), permanganate
3327	S	Fe(III), tartrate
3328	S <sup>2-</sup>	CN <sup>-</sup> , S <sup>2-</sup> , sulfite
3329	Sulfate	Permanganate + sulfuric acid, sulfur
3330	Sulfite	Cr(III) + heat
3331	SO <sub>6</sub> <sup>2-</sup>	HCHO, Hg(II), permanganate + sulfuric acid
3332	Se and its anions	Ascorbic acid, hydroxylamine, thiosulfate

Anion or Neutral Molecule	Masking Agent
TeI <sup>-</sup>	Diaminobenzidine, sulfide, sulfite
Tungstate	Citrate, tartrate
Vanadate	Tartrate

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(1) Compiled from Perrin (1979, p. 612) and Dean (1995)

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Demasking refers to any procedure that eliminates the effect of a masking agent already present in solution. There are a variety of methods for demasking, including changing the pH of the solution and physically removing, destroying, or displacing the masking agent. The stability of most metal complexes depends on pH, so simply raising or lowering the pH is frequently sufficient for demasking. Another approach to demasking involves the formation of new complexes or compounds that are more stable than the masked species. For example, boric acid commonly is used to demask the fluoride complexes of Sn<sup>4+</sup> or Mo<sup>6+</sup>, and hydroxide is used to demask the thiocyanate complexes of Fe<sup>3+</sup>. In addition, it might be possible to destroy the masking agent in solution through a chemical reaction (i.e., via the oxidation of EDTA in acidic solutions by permanganate or another strong oxidizing agent).

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#### 14.10.9 Review of Specific Radionuclides

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##### 14.10.9.1 Americium

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Americium is a metal of the actinide series which is produced synthetically by neutron activation of uranium or plutonium followed by beta decay.

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##### Isotopes

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Twenty isotopes of americium are known, <sup>232</sup>Am through <sup>248</sup>Am, including three metastable states. All isotopes are radioactive. <sup>243</sup>Am and <sup>241</sup>Am, alpha emitters, are the longest lived with a half-lives of 7,380 years and 432.7 years, respectively. <sup>241</sup>Am and <sup>243</sup>Am also undergo spontaneous fission. <sup>242m</sup>Am has a half-life of 141 years, and the half-lives of the remaining isotopes are measured in hours, minutes, or seconds. <sup>241</sup>Am is the most common isotope of environmental concern.

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##### Occurrence

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None of the isotopes of americium occur naturally. It is produced synthetically by neutron bombardment of <sup>238</sup>U or <sup>239</sup>Pu followed by beta decay of the unstable intermediates. <sup>241</sup>Am is

3361 found in military wastes and can be extracted from reactor wastes. Some industrial ionization  
3362 sources also contain americium. Decay of  $^{241}\text{Pu}$  injected in the atmosphere during weapons  
3363 testing contributes to the presence of  $^{241}\text{Am}$ .

3364 The silver metal is prepared by reduction of americium fluoride ( $\text{AmF}_3$ ) or americium oxide  
3365 ( $\text{AmO}_2$ ) with active metals at high temperatures and is purified by fractional distillation, taking  
3366 advantage of its exceptionally high vapor pressure compared to other transuranium elements.  
3367 Kilogram quantities of  $^{241}\text{Am}$  are available, but only 10 to 100 g quantities of  $^{243}\text{Am}$  are prepared.

3368 Soft gamma emission from  $^{241}\text{Am}$  is used to measure the thickness of metal sheets and metal  
3369 coatings, the degree of soil compaction, sediment concentration in streams, and to induce X-ray  
3370 fluorescence in chemical analysis. As an alpha emitter, it is mixed with beryllium to produce a  
3371 neutron source for oil-well logging and to measure water content in soils and industrial process  
3372 streams. The alpha source is also used to eliminate static electricity and as an ionization source in  
3373 smoke detectors.

#### 3374 Solubility of Compounds

3375 Among the soluble salts are the nitrate, halides, sulfate, and chlorate of americium(III). The  
3376 fluoride, hydroxide, and oxalate are insoluble. The phosphate and iodate are moderately soluble  
3377 in acid solution. Americium(VI) is precipitated with sodium acetate to produce the hydrate,  
3378  $\text{NaAmO}_2(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot x\text{H}_2\text{O}$ .

#### 3379 Review of Properties

3380 The study of the properties of americium is very difficult because of the intense alpha radiation  
3381 emitted by  $^{241}\text{Am}$  and  $^{243}\text{Am}$ , but some properties are known. Americium metal is very ductile  
3382 and malleable but highly reactive and unstable in air, forming the oxide. It is considered to be a  
3383 slightly more active metal than plutonium and is highly reactive combining directly with oxygen,  
3384 hydrogen, and halides to form the respective compounds,  $\text{AmO}_2$ ,  $\text{AmH}_3$ , and  $\text{AX}_3$ . Alloys of  
3385 americium with platinum, palladium, and iridium have been prepared by hydrogen reduction of  
3386 americium oxide in the presence of the finely divided metals.

3387 Unless the transuranium elements are associated with high-level gamma emission, the principal  
3388 toxicological problems associated with the radionuclides are the result of internal exposure after  
3389 inhalation or ingestion. When inhaled or ingested, they are about equally distributed between  
3390 bone tissue and the liver. At high doses transuranics lead to malignant tumors years later. In  
3391 addition, large quantities of  $^{241}\text{Am}$  could conceivably lead to criticality problems, producing

## Separation Techniques

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3392 external radiation hazards or neutron exposure from ( $\alpha$ ,n) reactions.  $^{241}\text{Am}$  is also a gamma  
3393 emitter.

3394 Americium is generally thought to be absorbed by all common rocks at pH values found in the  
3395 environment. Complexation of Am(III) by naturally occurring ligands, however, would be  
3396 expected to strongly reduce its adsorption.

### 3397 Solution Chemistry

3398 Americium can exist in solution in the +3, +4, +5, and +6 oxidation states. Simple aqueous ions  
3399 of  $\text{Am}^{+3}$  and  $\text{AmO}_2^{+2}$  (VI oxidation state) are stable in dilute acid, but  $\text{Am}^{+3}$  is the predominant  
3400 oxidation state. Free radicals produced by radiolysis of water by alpha particles reduce the higher  
3401 states spontaneously to  $\text{Am}^{+3}$ . The +3 oxidation state exists as  $\text{Am}(\text{OH})_3$  in alkaline solution.  
3402 Simple tetravalent americium is unstable in mineral acid solutions, disproportionating rapidly to  
3403 produce  $\text{Am}^{+3}$  and  $\text{AmO}_2^{+1}$  [Am(V)] in nitric and perchloric acid solutions. Conversely,  
3404 dissociation of  $\text{Am}(\text{OH})_4$  or  $\text{AmO}_2$  [both Am(IV)] in sulfuric acid solutions produces solutions  
3405 containing  $\text{Am}^{+3}$  and  $\text{AmO}_2^{+2}$ . Stability is provided by complexation with fluoride ions and  
3406 oxygen-containing ligands such as carbonate and phosphate ions. The  $\text{AmO}_2^{+1}$  ion also  
3407 disproportionates in acid solutions to yield  $\text{Am}^{+3}$  and  $\text{AmO}_2^{+2}$ , but the process for  $^{241}\text{Am}$  is so  
3408 slow that radiation-induced reduction dominates. Evidence exists for the presence of  $\text{Am}^{+7}$  in  
3409 alkaline solutions from the oxidation of  $\text{AmO}_2^{+2}$ .

3410 OXIDATION-REDUCTION BEHAVIOR. Although disproportionation reactions convert the +4 and +5  
3411 oxidation states into the +3 and +6 states, radiolysis eventually converts the higher oxidation  
3412 state into  $\text{Am}^{+3}$ . Redox processes are used, however, to produce solutions of alternate oxidation  
3413 states and to equilibrate the forms of americium into a common state, usually +3, but sometimes  
3414 +6.

3415 The +4 state is reduced to  $\text{Am}^{+3}$  by iodide. In dilute, non-reducing solutions, peroxydisulfate  
3416 ( $\text{S}_2\text{O}_8^{-2}$ ) oxidizes both the +3 and +5 states to the +6 state.  $\text{Ce}^{+4}$  and ozone ( $\text{O}_3$ ) oxidizes the +5  
3417 state to +6 in perchloric acid solution. Electrolytic oxidation of  $\text{Am}^{+3}$  to  $\text{AmO}_2^{+2}$  occurs in  
3418 phosphoric, nitric, and perchloric acid solutions and solutions of sodium bicarbonate ( $\text{Na}_2\text{CO}_3$ ).  
3419 The latter ion is reduced to  $\text{Am}^{+3}$  by iodide, hydrogen peroxide, and the nitrite ion ( $\text{NO}_2^{-1}$ ).

3420 COMPLEXATION. The +3 oxidation state forms complexes in the following order of strength (in  
3421 aqueous solution):  $\text{F}^- > \text{H}_2\text{PO}_4^- > \text{SCN}^- > \text{NO}_3^- > \text{Cl}^-$ . Both americium (+3) and (IV) form  
3422 complexes with organic chelants. These are stable in aqueous and organic solvents. Americium

3423 (IV) however can be easily reduced unless special oxidizing conditions are maintained.” The  
3424  $\text{AmO}_2^{+2}$  ion also forms significant complex ions with nitrate, sulfate, and fluoride ions.

3425 HYDROLYSIS. The actinide elements are known for their tendency to hydrolyze and, in many  
3426 cases, form insoluble polymers. In the predominant +3 oxidation state in solution, americium,  
3427 with its large radius, has the least tendency of the +3 actinides to hydrolyze; yet, hydrolysis is  
3428 expected to occur with some polymerization. Hydrolysis that does occur is complicated and  
3429 depends on the nature of the cations present and may start at pH values as low as 0.5-1.0. In  
3430 contrast, the  $\text{AmO}_2^{+2}$ , like all actinyl ions, undergoes hydrolysis to an appreciable extent. The  
3431 tendency to form polymers of colloidal dimensions, however, appears to be small relative to  
3432 other actinide ions in the +6 oxidation state. Precipitation occurs early on after relatively small  
3433 polymeric aggregates form in solution. The strong tendency to form insoluble precipitates after a  
3434 small amount of hydrolysis makes characterization of the water-soluble polymers a difficult  
3435 problem.

3436 RADIOCOLLOIDS. At trace concentrations, a colloidal form of  $\text{Am}^{+2}$  can easily be prepared, so  
3437 steps should be taken to avoid its formation during analytical procedures. At high pH ranges,  
3438 colloids form from the  $\text{Am}(\text{OH})_3$ , and at lower pH ranges through adsorption of  $\text{Am}^{+3}$  onto  
3439 foreign particles. Their formation depends on storage time, pH, and ionic strength of the solution.

#### 3440 Dissolution of Samples

3441 Americium is generally dissolved from irradiated reactor fuels, research compounds, and soil,  
3442 vegetation, and biological samples. Spent fuel elements may be difficult to dissolve but  
3443 eventually yield to digestion with hydrofluoric acid, nitric acid, or sulfuric acid. Aqua regia is  
3444 used if platinum is present, and hydrochloric acid with an oxidizing agent such as sodium  
3445 chlorate. Perchloric acid, while a good solvent for uranium, reacts too vigorously. Sodium  
3446 hydroxide-peroxide is a good basic solvent. Research compounds, usually salts, yield to hot  
3447 concentrated nitric or sulfuric acid. Soil samples are digested with concentrated nitric acid,  
3448 hydrofluoric acid, or hydrochloric acid. Vegetation and biological samples are commonly wet  
3449 ashed, and the residue is treated with nitric acid.

#### 3450 Separation Methods

3451 The separation of americium, particularly from other transuranics, is facilitated by the  
3452 exceptional stability of  $\text{Am}(\text{III})$  compared to the trivalent ions of other actinides, which more  
3453 readily convert to higher oxidation states under conditions that americium remains trivalent.

3454 PRECIPITATION AND COPRECIPITATION. Coprecipitation with lanthanum fluoride ( $\text{LaF}_3$ ) is  
3455 achieved after reduction of higher oxidation states to Am(III). Select oxidation of other  
3456 transuranic elements such as neptunium and plutonium to the IV or VI oxidation states  
3457 solubilizes these radionuclides leaving americium in the insoluble form. Although coprecipita-  
3458 tion with rare earths as fluorides or hydroxides from a bicarbonate solution of americium(VI), is  
3459 used to purify americium, it is not as effective as ion-exchange procedures. Other coprecipitating  
3460 agents for americium(III) include thorium oxalate [ $\text{Th}(\text{C}_2\text{O}_4)_2$ ], calcium oxalate ( $\text{CaC}_2\text{O}_4$ ), ferric  
3461 hydroxide [ $\text{Fe}(\text{OH})_3$ ], and lanthanum potassium sulfate [ $\text{LaK}(\text{SO}_4)_2$ ]. Americium(IV) is also  
3462 coprecipitated with these reagents as well as with zirconium phosphate [ $\text{Zr}_3(\text{PO}_4)_2$ ].  
3463 Americium(VI) is not coprecipitated with any of these reagents but with sodium uranyl acetate  
3464 [ $\text{NaUO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ ].

3465 SOLVENT EXTRACTION. Organic solvents and chelating agents are available for separating  
3466 americium from other radionuclides by selectively extracting either americium or the alternate  
3467 radionuclide from aqueous solutions into an organic phase. Tributyl phosphate (TBP) in kerosene  
3468 or thenoyltrifluoroacetone (TTA) in xylene removes most oxidation states of neptunium and  
3469 plutonium from americium(III) in the presence of dilute nitric acid. The addition of sodium  
3470 nitrate (6 M) tends to reverse the trend making americium more soluble in TBP than uranium,  
3471 neptunium, or plutonium radionuclides. Di(2-ethylhexyl)phosphoric acid (HDEHP) in toluene is  
3472 highly effective in extracting americium(III) and is used in sample preparation for alpha  
3473 spectroscopic analysis.

3474 Recently, solvent extraction chromatography has offered an efficient, easy technique for rapidly  
3475 separating americium and other transuranic elements. A process using octylphenyl-N,N-  
3476 diisobutyl carbamoylphosphine oxide (CMPO) in dissolved TBP and fixed on an inert polymeric  
3477 resin matrix has been used to isolate americium(III). The column is loaded with 2 M nitric acid,  
3478 and americium is eluted with 4 M hydrochloric acid. It is important to note that iron, found in  
3479 most environmental samples, does not effect the americium isolation if the iron is kept in the +2  
3480 oxidation state. The ferric ion ( $\text{Fe}^{+3}$ ) is detrimental to the separation.

3481 ION EXCHANGE. Separation of americium can be achieved by cation-exchange chromatography.  
3482 Any of its oxidation states absorb on a cation resin in dilute acid solution, but the higher  
3483 oxidation states are not important in cation-exchange separations because they are unstable  
3484 toward reduction to the +3 state. Generally, americium(III) is the last tripositive ion among the  
3485 actinides eluted from a cation-exchange matrix, although the order may not be maintained under  
3486 all conditions. Many eluting agents are available for specific separations. Concentrated  
3487 hydrochloric acid, for example, has been used for separating actinides such as americium from  
3488 the lanthanides. Anion-exchange chromatography has been widely used for separating

3489 americium. Anionic complexes of americium(III) form at high chloride concentrations, providing  
3490 a chemical form that is easily exchanged on an anion-exchange column. The column can be  
3491 eluted using dilute hydrochloric acid or a dilute hydrochloric acid/ammonium thiocyanate  
3492 solution. Anion-exchange separations of americium are also realized with columns prepared with  
3493 concentrated nitric acid solutions. The sequential separation of the actinides is accomplished  
3494 readily using anion-exchange chromatography. Americium, plutonium, neptunium, thorium,  
3495 protactinium, curium, and uranium can all be separated by the proper application of select acid or  
3496 salt solutions to the column.

3497 ELECTRODEPOSITION. Americium can be electrodeposited for alpha spectrometry measurement  
3498 on a highly-polished platinum cathode. The sample is dissolved in a dilute hydrochloric acid  
3499 solution that has been adjusted to a pH of about six with ammonium hydroxide solution using  
3500 methyl red indicator. The process runs for one hour at 1.2 amps.

#### 3501 Methods of Analysis

3502 <sup>241</sup>Am is detected and quantified by either alpha counting or gamma spectroscopy. Trace  
3503 quantities of <sup>241</sup>Am are analyzed by alpha counting, after separation from interfering  
3504 radionuclides by solvent extraction, coprecipitation, or ion-exchange chromatography. The  
3505 isolated radionuclide is collected by coprecipitation, filtered, and mounted on a planchet or  
3506 electroplated onto a platinum electrode for counting by alpha spectrometry. <sup>243</sup>Am is added to the  
3507 analytical solution as a tracer to measure chemical recovery. <sup>241</sup>Am in bulk soil samples can be  
3508 determined by gamma spectroscopy.

3509 Compiled from: Ahrland, 1986; Baes and Mesmer, 1976; Choppin et al., 1995; Considine  
3510 and Considine, 1983; Cotton and Wilkinson, 1988; DOE, 1990 and 1997, 1995; 1997;  
3511 Ehmann and Vance, 1991; Greenwood and Earnshaw, 1984; Haissinsky and Adolff, 1965;  
3512 Katz et al., 1986; Lindsay, 1988; Metz and Waterbury, 1962; NEA, 1982; SCA, 2001;  
3513 Penneman, 1994; Penneman and Keenan, 1960; Schulz and Penneman, 1986; Seaborg and  
3514 Loveland, 1990; Horwitzetal, 1993.

#### 3515 14.10.9.2 Cesium

3516 Cesium is the last member of the naturally occurring alkali metals in group IA of the periodic  
3517 table with an atomic number of 55. As such, its radiochemistry is simplified because the Group  
3518 IA metals form only +1 ions. Elemental cesium is a very soft, silver-white metallic solid in the  
3519 pure state with a melting point of only 28.5 °C. It tarnishes quickly to a golden-yellow color

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3520 when exposed to small amounts of air. In larger amounts of air it ignites spontaneously. It is  
3521 normally stored under xylente/toluene to prevent contact with air.

### 3522 Isotopes

3523 Cesium isotopes of mass number 112 to 148 have been identified.  $^{133}\text{Cs}$  is the only stable isotope.  
3524  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  are the only two isotopes of significance from an environmental perspective. Both  
3525 are formed from the nuclear fission process. Their half-lives are 2.06 and 30.17 years,  
3526 respectively.

### 3527 Occurrence

3528 Cesium is widely distributed in the Earth's crust with other alkali metals. In granite and  
3529 sedimentary rocks the concentration is less than 7 ppm. In seawater it is about 0.002 ppm, but in  
3530 mineral springs the concentration may be greater than 9 mg/L. Cesium is found in complex  
3531 minerals such as carnallite, a potassium and magnesium chloride mineral that contains small  
3532 percentages of cesium compounds; lepidolite ores, a lithium aluminum silicate; and pollucite, a  
3533 cesium-rich ore of the oxides of cesium, aluminum, and silicon.  $^{137}\text{Cs}$  is produced in nuclear  
3534 fission and occurs in atmospheric debris from weapons tests and accidents. It is a very important  
3535 component of radioactive fallout; and because of its moderately long half-life and high solubility,  
3536 it is a major source of long-lived external gamma radiation from fallout. It accounts for 30  
3537 percent of the gamma activity of fission products stored for one year, 70 percent in two years,  
3538 and 100 percent after five years.

3539 Cesium metal is not produced on a commercial scale. It is isolated from its minerals, however, by  
3540 acid extraction, fusion with alkaline fluxes, or direct reduction of an ore to metallic cesium.  
3541 Extraction and fusion yield a cesium salt, which is treated by oxidation-reduction processes to  
3542 make the pure metal. The salt is either roasted with carbon, heated with calcium or lithium, or  
3543 electrolyzed as a melt to reduce the cation to pure cesium. Special equipment should be used in  
3544 these processes because of the very reactive chemical nature of the metal.

3545 Metallic cesium is used in photoelectric cells, spectrographic instruments, scintillation counters,  
3546 and other optical and detecting devices, sometimes alloyed with calcium, strontium, or barium to  
3547 facilitate handling. Its most recognized use is in the atomic clock that serves to define the second.  
3548 Cesium has been considered as a fuel in ion-propulsion engines for deep space travel and as a  
3549 heat-transfer medium for some applications.  $^{137}\text{Cs}$  has replaced  $^{60}\text{Co}$  in the treatment of cancer  
3550 and has been used in industrial radiography for the control of welds. Cesium compounds are used  
3551 in glass and ceramic production, as an absorbent in carbon dioxide production plants, and in the

3552 preparation of density gradients for the separation of macromolecules by centrifugation.  $^{37}\text{Cs}$  is  
3553 also used commercially as a sealed source in liquid scintillation spectrometers. The 661 keV  
3554 gamma ray it emits is used to create an electron (Compton effect) distribution which allows the  
3555 degree of sample quench to be determined.

#### 3556 Solubility of Compounds

3557 Most cesium salts are very soluble in water and dilute acids. Among the salts of common anions,  
3558 the notable exceptions are cesium perchlorate and periodate ( $\text{CsClO}_4$  and  $\text{CsIO}_4$ ). Several cesium  
3559 compounds of large anions are insoluble. Examples include the following: silicotungstate  
3560 [ $\text{Cs}_8\text{SiW}_{12}\text{O}_{42}$ ], permanganate ( $\text{CsMnO}_4$ ), chloroplatinate ( $\text{Cs}_2\text{PtCl}_6$ ), tetraphenylborate  
3561 [ $\text{CsB}(\text{C}_6\text{H}_5)_4$ ], alum [ $\text{CsAl}(\text{SO}_4)_2$ ], and cobaltnitrate complex [ $\text{Cs}_3\text{Co}(\text{NO}_3)_6$ ].

#### 3562 Review of Properties

3563 Cesium is the most active and electropositive of all the metals. It forms compounds with most  
3564 inorganic and organic anions; it readily forms alums with all the trivalent cations that are found  
3565 in alums. The metal readily ionizes, and in ammonia solutions and it is a powerful reducing  
3566 agent. When exposed to moist air, it tarnishes initially forming oxides and a nitride and then  
3567 quickly melts or bursts into flame. With water the reaction is violent. Cesium reacts vigorously  
3568 with halogens and oxygen, and it is exceptional among the alkali metals in that it can form stable  
3569 polyhalides such as  $\text{CsI}_3$ . Reaction with oxygen forms a mixture of oxides: cesium oxide ( $\text{Cs}_2\text{O}$ ),  
3570 cesium peroxide ( $\text{Cs}_2\text{O}_2$ ), and cesium superoxide ( $\text{CsO}_2$ ). The toxicity of cesium compounds is  
3571 generally not important unless combined with another toxic ion.

3572  $^{137}\text{Cs}$ , introduced into the water environment as cations, is attached to soil particles and can be  
3573 removed by erosion and runoff. However, soil sediment particles act as sinks for  $^{137}\text{Cs}$ , and the  
3574 radionuclide is almost irreversible bound to mica and clay minerals in freshwater environments.  
3575 It is unlikely that  $^{137}\text{Cs}$  will be removed from these sediments under typical environmental  
3576 conditions. Solutions of high ionic strength as occur in estuarine environments might provide  
3577 sufficient exchange character to cause cesium to become mobile in the ecosphere.

#### 3578 Solution Chemistry

3579 The cesium ion exists in only the +1 oxidation state, and its solution chemistry is not complicated  
3580 by oxidation-reduction reactions. As a result, it undergoes complete, rapid exchange with carriers  
3581 in solution. The cesium ion is colorless in solution and is probably hydrated as a hexaquo  
3582 complex.

## Separation Techniques

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3583 COMPLEXATION. Cesium ions form very few complex ions in solution. The few that form are  
3584 primarily with nitrogen-donor ligands or beta-diketones. Anhydrous beta-diketones are insoluble  
3585 in water, but in the presence of additional coordinating agents, including water, they become  
3586 soluble in hydrocarbons. One solvent-extraction procedure from aqueous solutions is based on  
3587 chelation of cesium with 1,1,1-trifluoro-3-(2'-thenoyl)acetone (TTA) in a hydrocarbon solvents.  
3588 Cesium is sandwiched between crown ligands, associated with the oxygen atoms of the ether, in  
3589  $[\text{Cs}_9(18\text{-C-}6)_{14}]^{+9}$ .

3590 HYDROLYSIS. With the small charge and large radius of the cesium ion, hydrolysis reactions are  
3591 inconsequential.

3592 ADSORPTION. When cesium is present in extremely low concentrations, even in the presence of 2  
3593 M acid, adsorption on the walls of glass and plastic containers leads to complications for the  
3594 radioanalyst. Half the activity of cesium radionuclides, for example, can be lost from acid  
3595 solutions stored for one month in these containers. Experiments indicate that addition of 1  $\mu\text{g}$   
3596 cesium carrier per mL of solution is sufficient to stabilize acid solutions for six months.

### 3597 Dissolution of Samples

3598 Radiochemists generally dissolve cesium samples from irradiated nuclear fuel, activated cesium  
3599 salts, natural water, organic material, agriculture material, and soils. Nuclear fuel samples are  
3600 generally dissolved in HCl, HNO<sub>3</sub>, HF, or a combination of these acids. Care should be taken to  
3601 ensure that the sample is representative if <sup>137</sup>Cs has been used as a burn-up monitor. Precautions  
3602 should also be taken with these samples to prevent loss of cesium because of leaching or  
3603 incomplete sample dissolution. Most cesium salts dissolve readily in water and acid solutions. In  
3604 water samples, the cesium might require concentration, preferably by ion exchange, or by  
3605 precipitation or coprecipitation if interfering ions are present. Organic materials are either  
3606 decomposed by HNO<sub>3</sub> or dry ashed, and the cesium is extracted with hot water or hot acid  
3607 solution. Extraction and leaching procedure have been use to assess exchangeable or leachable  
3608 cesium using ammonium acetate solutions or acid solutions, but soils are generally completely  
3609 solubilized in HNO<sub>3</sub>, HCl, HF, H<sub>2</sub>SO<sub>4</sub>, or a mixture of these acids in order to account for all the  
3610 cesium in a soil sample.

### 3611 Separation Methods

3612 PRECIPITATION AND COPRECIPITATION. Cesium is separated and purified by several precipitation  
3613 and coprecipitation methods using salts of large anions. Gravimetric procedures rely on  
3614 precipitation to collect cesium for weighing, and several radiochemical techniques isolate cesium

3615 radionuclides for counting by precipitation or coprecipitation. Cesium can be precipitated, or  
3616 coprecipitated in the presence of cesium carrier, by the chlorate, cobaltinitrate, platinate, and  
3617 tetraphenylborate ions. Other alkali metals interfere and should be removed before a pure  
3618 insoluble compound can be collected. Cesium can be isolated from other alkali metals by  
3619 precipitation as the silicotungstate. The precipitate can be dissolved in 6 M sodium hydroxide,  
3620 and cesium can be further processed by other separation procedures. The tetraphenylborate  
3621 procedure first removes other interfering ions by a carbonate and hydroxide precipitation in the  
3622 presence of iron, barium, lanthanum, and zirconium carriers. Cesium is subsequently precipitated  
3623 by the addition of sodium tetraphenylborate to the acidified supernatant. Alum also precipitates  
3624 cesium from water samples in the presence of macro quantities of the alkali metals. Trace  
3625 quantities of cesium radionuclides are precipitated using stable cesium as a carrier.

3626 ION EXCHANGE. The cesium cation is not retained by anion-exchange resins and does not form a  
3627 suitable anion for anion-exchange chromatography. The process is used, however, to separate  
3628 cesium from interfering ions that form anionic complexes. Cesium elutes first in these  
3629 procedures. Cesium is retained by cation-exchange resins. Because the cesium ion has the largest  
3630 ionic radius and has a +1 charge, it is less hydrated than most other cations. Therefore, cesium  
3631 has a small hydrated radius and can approach the cation exchange site to form a strong  
3632 electrostatic association with the ion-exchange resin. Binding of alkali metal ion to cation  
3633 exchange resins follows the order:  $Cs^{+1} > Rb^{+1} > K^{+1} > Na^{+1} > Li^{+1}$ . Cesium is generally the last alkali  
3634 metal ion to elute in cation-exchange procedures. In some procedures, the process is not  
3635 quantitative after extensive elution.

3636 SOLVENT EXTRACTION. Cesium does not form many complex ions, and solvent extraction is not  
3637 a common procedure for its separation. One solvent-extraction procedure, however, is based on  
3638 chelation of cesium with 1,1,1-trifluoro-3-(2'-thenoyl)acetone (TTA) in a solvent of methyl  
3639 nitrate/hydrocarbons. Cesium can also be extracted from fission product solutions with sodium  
3640 tetraphenylborate in amyl acetate. It can be stripped from the organic phase by 3 M HCl.

#### 3641 Methods of Analysis

3642 Macroscopic quantities of cesium have been determined by gravimetric procedures using one of  
3643 the precipitating agents described above. Spectrochemical procedures for macroscopic quantities  
3644 include flame photometry, emission spectroscopy, and X-ray emission.

3645 Gamma ray spectrometry allows detection of  $^{134}Cs$ ,  $^{136}Cs$ , and  $^{137}Cs$  down to very low levels. The  
3646 gamma ray measured for  $^{137}Cs$  (661 Kev) actually is emitted from its progeny  $^{136m}Ba$ . However,  
3647 since the half-life of the barium isotope is so short (2.5 min) it is quickly equilibrated with its

3648 parent cesium isotope (i.e., secular equilibrium).  $^{137}\text{Cs}$  is used as part of a group of nuclides in a  
3649 mixed radioactivity source for calibration of gamma ray spectrometers.

3650 Compiled from: Choppin et al., 1995; Considine and Considine, 1983; Cotton and  
3651 Wilkinson, 1988; Emsley, 1989; EPA, 1973; EPA, 1973; EPA, 1980; Finston and Kinsley,  
3652 1961; Friedlander et al., 1981; Hampel, 1968; Hassinsky and Adolff, 1965; Kallmann, 1964;  
3653 Lindsay, 1988; Sittig, 1994.

#### 3654 14.10.9.3 Cobalt

3655 Cobalt, atomic number 27, is a silvery-grey, brittle metal found in the first row of the transition  
3656 elements in the periodic table, between iron and nickel. Although it is in the same family of  
3657 elements as rhodium and iridium, it resembles iron and nickel in its free and combined states.

#### 3658 Isotopes

3659  $^{59}\text{Co}$  is the only naturally occurring isotope of the element. The other twenty-two isotopes and  
3660 their metastable states, ranging from mass numbers 50 to 67, are radioactive. Isotopes with mass  
3661 numbers less than 59 decay by positron emission or electron capture. Isotopes with mass  
3662 numbers greater than 59 decay by beta and gamma emission. Except for  $^{60}\text{Co}$ , the most important  
3663 radionuclide, their half-lives range from milliseconds to days. The principle isotopes of cobalt  
3664 (with their half-lives) are  $^{57}\text{Co}$  (272 d),  $^{58}\text{Co}$  (71 d), and  $^{60}\text{Co}$  (5.27 y). Isotopes 57 and 58 can be  
3665 determined by X-ray as well as gamma spectrometry. Isotope 60 is easily determined by gamma  
3666 spectrometry.

#### 3667 Occurrence and Uses

3668 The cobalt content of the crust of the earth is about 30 ppm, but the element is widely distributed  
3669 in nature, found in soils, water, plants and animals, meteorites, stars, and lunar rocks. Over 200  
3670 cobalt minerals are known. Commercially, the most important are the arsenides, oxides, and  
3671 sulfides. Important commercial sources also include ores of iron, nickel, copper, silver,  
3672 manganese, and zinc.  $^{60}\text{Co}$  is produced by neutron activation of stable  $^{59}\text{Co}$ .  $^{56}\text{Co}$  and  $^{57}\text{Co}$  are  
3673 prepared by bombardment of iron or nickel with protons or deuterons.

3674 Some of the metallic cobalt is isolated from its minerals, but much of the metal is produced  
3675 primarily as a byproduct of copper, nickel, or lead extraction. The processes are varied and  
3676 complicated because of the similar chemical nature of cobalt and the associated metals.

3677 Since ancient times cobalt ores has been used to produce the blue color in pottery, glass, and  
3678 ceramics. Cobalt compounds are similarly used as artist pigments, inks, cotton dyes, and to speed  
3679 the drying of paints and inks. They also serves as catalysts in the chemical industry and for  
3680 oxidation of carbon monoxide in catalytic converters. One of the major uses of cobalt is the  
3681 preparation of high-temperature or magnetic alloys. Jet engines and gas turbines are  
3682 manufactured from metals with a high content of cobalt (up to 65 percent) alloyed with nickel,  
3683 chromium, molybdenum, tungsten, and other metals.

3684 Little use if made of pure cobalt except as a source of radioactivity from  $^{60}\text{Co}$ . The radionuclide  
3685 is used in cancer radiotherapy, as a high-energy gamma source for the radiography of metallic  
3686 objects, fluids, and other solids, or as an injectable radionuclide for the measurement of flow  
3687 rates in pipes.

#### 3688 Solubility of Compounds

3689 Most simple cobalt compounds contain cobalt (II), but cobalt (II) and cobalt(III) display varied  
3690 solubilities in water. To some extent, their solubilities depend on the oxidation state of the metal.  
3691 For example, all the halides of cobalt (II) are soluble but the only stable halide of cobalt (III), the  
3692 fluoride, is insoluble. The sulfates of both oxidation states are soluble in water. The acetate of  
3693 cobalt (II) is soluble, but that of cobalt (III) hydrolyses in water. The bromate, chlorate, and  
3694 perchlorate of cobalt (II) are also soluble. Insoluble compounds include all the oxides of both  
3695 oxidation states, cobalt (II) sulfide, cyanide, oxalate, chromate, and carbonate. The hydroxides  
3696 are slightly soluble. Several thousand complex compounds of cobalt are known. Almost all are  
3697 cobalt (III) complexes and many are soluble in water.

#### 3698 Review of Properties

3699 Metallic cobalt is less reactive than iron and is unreactive with water or oxygen in air unless  
3700 heated, although the finely divided metal is pyrophoric in air. On heating in air it forms the  
3701 oxides, cobalt (II) oxide ( $\text{CoO}$ ) below  $200\text{ }^{\circ}\text{C}$  and above  $900\text{ }^{\circ}\text{C}$  and cobalt (II)-cobalt (III) oxide  
3702 ( $\text{Co}_3\text{O}_4$ ) between the temperatures. It reacts with common mineral acids and slowly with  
3703 hydrofluoric and phosphoric acids to form cobalt (II) salts and with sodium and ammonium  
3704 hydroxides. On heating, it reacts with halogens and other nonmetals such as boron, carbon,  
3705 phosphorus, arsenic, antimony, and sulfur.

3706 Cobalt exists in all oxidation states from -1 to +4. The most common are the +2 and +3 oxidation  
3707 states. The +1 state is found in a several complex compounds, primarily the nitrosyl and carbonyl  
3708 complexes and certain organic complexes. The +4 state exist in some fluoride complexes.

## Separation Techniques

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3709 Cobalt(II) is more stable in simple compounds and is not easily hydrolyzed. Few simple  
3710 compounds are known for the +3 state, but cobalt is unique in the numerous stable complex  
3711 compounds it forms.

3712 The toxicity of cobalt is not comparable to metals such as mercury, cadmium, or lead. Inhalation  
3713 of fine metallic dust can cause irritation of the respiratory system, and cobalt salts can cause  
3714 benign dermatosis. <sup>60</sup>Co is made available in various forms, in sealed aluminum or monel  
3715 cylinders for industrial applications, as wires or needles for medical treatment, and in various  
3716 solid and solution forms for industry and research. Extreme care is required in handling any of  
3717 these forms of cobalt because of the high-energy gamma radiation from the source.

### 3718 Solution Chemistry

3719 In aqueous solution and in the absence of complexing agents, cobalt (II) is the only stable  
3720 oxidation state, existing in water as the pink-red hexaquo complex ion,  $\text{Co}(\text{H}_2\text{O})_6^{+2}$ . Simple  
3721 cobalt ions in the +3 oxidation state decompose water in an oxidization-reduction process that  
3722 generates cobalt (II):



3724 Complexation of cobalt (III) decreases its oxidizing power and most complex ions of the +3  
3725 oxidation state are stable in solution.

3726 COMPLEXATION. Several thousand complexes of cobalt have been prepared and extensively  
3727 studied, including neutral structures and those containing complex cations and/or anions. Among  
3728 these, the cobalt (III) complexes are the strongest and represent one of the largest groups of  
3729 complex compounds. The most common cobalt (III) compounds contain six ligands bonded to  
3730 the metal atom or cation (coordination number six) in an octahedral arrangement. It forms many  
3731 complex ions with nitrogen-compounds such as ammonia and amines ( $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ) by  
3732 coordinating through the nitrogen atom, and with those containing carbon ( $\text{K}_3[\text{Co}(\text{CN})_6]$ ), oxygen  
3733 and sulfur ( $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$ ), and halides ( $\text{Na}_3[\text{CoF}_6]$ ). Complex compounds with mixed ligands  
3734 are common:  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$  and  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ .

3735 The +2 oxidation state forms complexes with a coordination of four or six, and in aqueous  
3736 solution,  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  is in equilibrium with some  $[\text{Co}(\text{H}_2\text{O})_4]^{+2}$ . In alkaline solution  $\text{Co}^{+2}$   
3737 precipitates as  $\text{Co}(\text{OH})_2$ , but the ion is amphoteric; and in concentrated hydroxide solutions, the  
3738 precipitate dissolves forming  $[\text{Co}(\text{OH})_4]^{-2}$ . Many complexes of the form  $[\text{Co}(\text{X})_4]^{-1}$  exist with  
3739 monodentate anionic ligands such as  $\text{Cl}^{-1}$ ,  $\text{Br}^{-1}$ ,  $\text{I}^{-1}$ ,  $\text{SCN}^{-1}$ ,  $\text{N}_3^{-1}$ , and  $\text{OH}^{-1}$ . Many aquo-halo

3740 complexes are known; they are various shades of red and blue. The aquo complex,  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$ ,  
3741 is pink.

3742 Chelate complexes are well-known and are used to extract cobalt from solutions of other ions.  
3743 Acetylacetone (acac) is used, for example, in a procedure to separate cobalt from nickel.  $\text{Co}^{+2}$  and  
3744  $\text{Ni}^{+2}$  do not form chelates with the acac,  $\text{Co}^{+3}$  does, however, and can be easily extracted.

3745 OXIDATION-REDUCTION BEHAVIOR. Most simple cobalt +3 compounds are unstable because the  
3746 +3 state is a strong oxidizing agent. It is very unstable in aqueous media, rapidly reducing to the  
3747 +2 state at room temperature. The aqueous ion of cobalt(II),  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$ , can be oxidized,  
3748 however, to the +3 state either by electrolysis or by ozone ( $\text{O}_3$ ) in cold perchloric acid ( $\text{HClO}_4$ );  
3749 solutions at 0 °C have a half-life of about one week. Compounds of the cobalt(III) complex ions  
3750 are formed by oxidizing the +2 ion in solution with oxygen or hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the  
3751 presence of ligands. The cobalt(III) hexamine complex forms according to:



3753 HYDROLYSIS. The hydrolysis of the +2 oxidation state of cobalt is not significant in aqueous  
3754 media below pH 7. At pH 7, hydrolysis of 0.001 M solution of the cation begins and is  
3755 significant at a pH above 9. The hydrolysis of the +3 oxidation state is reminiscent of the  
3756 hydrolysis of iron (III), but it is not as extensive. Hydrolysis of cobalt (III) is significant at pH 5.  
3757 In contrast, the hydrolysis of iron (III) becomes significant at a pH of about 3.

3758 Dissolution of Samples

3759 Cobalt minerals, ores, metals, and alloys can be dissolved by treatment first with hydrochloric  
3760 acid, followed by nitric acid. The insoluble residue remaining after application of this process is  
3761 fused with potassium pyrosulfate and sodium carbonate. In extreme cases, sodium peroxide  
3762 fusion is used. Biological samples are dissolved by wet ashing, digesting with heating in a  
3763 sulfuric-perchloric-nitric acid mixture.

3764 Separation Methods

3765 PRECIPITATION AND COPRECIPITATION. Cobalt can be precipitated by hydrogen sulfide ( $\text{H}_2\text{S}$ ),  
3766 ammonium sulfide ( $\text{NH}_4\text{S}$ ), basic acetate ( $\text{C}_2\text{H}_3\text{O}_2^{-1}/\text{HO}^{-1}$ ), barium carbonate ( $\text{BaCO}_3$ ), zinc oxide  
3767 ( $\text{ZnO}$ ), potassium hydroxide and bromine ( $\text{KOH}/\text{Br}_2$ ), ether and hydrochloric acid [ $(\text{C}_2\text{H}_5)_2\text{O}$  and  
3768  $\text{HCl}$ ], and cupferron. Cobalt sulfide ( $\text{CoS}$ ) is coprecipitated with stannic sulfide ( $\text{SnS}_2$ ) when

## Separation Techniques

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- 3769 low-solubility sulfides are precipitated in mineral acids. Care should be taken to avoid  
3770 coprecipitation of zinc sulfide (ZnS).
- 3771 Cobalt can be separated from other metals by hydroxide precipitation using pH control to  
3772 selectively precipitate metals such as chromium, zinc, uranium, aluminum, tin, iron (+3),  
3773 zirconium, and titanium at low pH. Cobalt precipitates at pH 6.8, and magnesium, mercury,  
3774 manganese, and silver at a pH greater than 7. Cobalt is not be separated from metals such as iron,  
3775 aluminum, titanium, zirconium, thorium, copper, and nickel using ammonium hydroxide  
3776 (NH<sub>4</sub>OH) solutions (aqueous ammonia), because an appreciable amount of cobalt is retained by  
3777 the hydroxide precipitates of these metals produced using this precipitating agent. Various  
3778 precipitating agents can be used to remove interfering ions prior to precipitating cobalt: iron by  
3779 precipitating with sodium phosphate (Na<sub>3</sub>PO<sub>4</sub>) or iron, aluminum, titanium, and zirconium with  
3780 zinc oxide.
- 3781 The separation of cobalt from interfering ions can be achieved by the quantitative precipitation of  
3782 cobalt with excess potassium nitrite (KNO<sub>2</sub>) to produce K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] (caution -- unstable to  
3783 heating after standing for some time). Ignition can be used to collect the cobalt as its mixed oxide  
3784 (Co<sub>3</sub>O<sub>4</sub>). Cobalt can also be precipitated with α-nitroso-β-naphthol (1-nitroso-2-naphthol) to  
3785 separate it from interfering metals. Nickel can interfere with this precipitation, but can be  
3786 removed with dimethylglyoxime. Precipitation as mercury tetracyanocobaltate (II)  
3787 {Hg[Co(SCN)<sub>4</sub>]} also is used, particularly for gravimetric analysis, and precipitation with  
3788 pyridine in thiocyanate solution is a quick gravimetric product, [Co(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>](SCN)<sub>2</sub>.
- 3789 SOLVENT EXTRACTION. Various ions or chelates have been used in solvent extraction systems to  
3790 isolate cobalt from other metals. Separation has been achieved by extracting either cobalt itself  
3791 or, conversely, extracting contaminating ions into an organic solvent in the presence of  
3792 hydrofluoric acid (HF), hydrochloric acid, and calcium chloride (HCl/CaCl<sub>2</sub>), hydrobromic acid  
3793 (HBr), hydroiodic acid (HI), or ammonium thiocyanate (NH<sub>4</sub>SCN). For example, cobalt (II) has  
3794 been separated from nickel (II) by extracting a hydrochloric acid solution containing calcium  
3795 chloride with 2-octanol. The ion is not extracted by diethyl ether from hydrobromic acid  
3796 solutions, but it is extracted from ammonium thiocyanate solutions by oxygen-containing organic  
3797 solvents in the presence of iron (III) by first masking the iron with citrate.
- 3798 Several chelate compounds have been used to extract cobalt from aqueous solutions.  
3799 Acetylacetone (acac) forms a chelate with cobalt (III), but not cobalt (II), that is soluble in  
3800 chloroform at pH 6 to 9, permitting separation from several metals including nickel. Cobalt (II)  
3801 can be oxidized to cobalt (III) with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) prior to extraction. α-nitroso-β-  
3802 naphthol has also been used as a chelating agent in the separation of cobalt (III) by solvent

3803 extraction. Diphenylthiocarbazone (dithiozone) has been used at pH 8 to extract cobalt into  
3804 carbon tetrachloride and chloroform after metals that form dithiozonates in acid solution (pH 3-  
3805 4) have been removed. 8-quinolinol has been used in a similar manner at pH up to 10. Masking  
3806 agents added to the system impede the extraction of iron, copper, and nickel.

3807 ION-EXCHANGE CHROMATOGRAPHY. Anion-exchange resins have been used extensively to  
3808 separate cobalt from other metals. The chloro-metal complexes, prepared and added to columns  
3809 in molar hydrochloric acid solutions, are eluted at varying concentrations of hydrochloric acid.  
3810 Trace amounts of <sup>59</sup>Fe, <sup>60</sup>Co, and <sup>65</sup>Zn and their respective carriers have been separated from  
3811 neutron-irradiated biological tissue ash with a chloride system. <sup>60</sup>Co has been eluted carrier-free  
3812 from similar samples and columns prepared with hydrobromic acid. Cobalt and contaminated  
3813 metals in nitric-acid systems behave in a manner similar to hydrochloric-acid systems. Cobalt  
3814 (II)-cyanide and cyanate complexes have been used to separate cobalt from nickel. The basic  
3815 form of quaternary amine resins (the neutral amine form) has been used in the column  
3816 chromatography of cobalt. Both chloride- and nitrate-ion systems have resulted in the association  
3817 of cobalt as a complex containing chloride or nitrate ligands as well as the neutral (basic)  
3818 nitrogen atom of the amine resin. Resins incorporating chelates in their matrix system have been  
3819 used to isolate cobalt. 8-quinolinol resins are very effective in separating cobalt from copper.

3820 ABSORBENT CHROMATOGRAPHY. Several inorganic adsorbents such as alumina, clays, and silica  
3821 are used to separate cobalt. Complex ions of cobaltamines separate on alumina as well as cobalt  
3822 (II) complexes of tartaric acid and dioxane. A complex of nitroso-R-salts are absorbed onto an  
3823 alumina column while other metals pass through the column. Cobalt is eluted with sulfuric acid.  
3824 Cobalt dithizonates absorb on alumina from carbon tetrachloride solutions. Cobalt is eluted with  
3825 acetone. The separation of cobalt from iron and copper has been achieved on aluminum  
3826 hydroxide [Al(OH)<sub>3</sub>]. Clay materials, kalolinite, benotite, and montmorilloite, separate cobalt (II)  
3827 from copper (II). Copper (II) absorbs and cobalt (II) elutes with water. Silica gel and activated  
3828 silica have both been used as adsorbents in cobalt chromatography.

3829 Organic adsorbents such as 8-hydroxyquinoline and dimethylglyoxime have been used in cobalt-  
3830 absorbent chromatographic systems. Powdered 8-hydroxyquinoline separates cobalt (II) from  
3831 other cations and anions, for example, and dimethylglyoxime separates cobalt from nickel.  
3832 Cobalt-cyano complexes absorb on activated charcoal, and cobalt is eluted from the column  
3833 while the anionic complexes of metals such as iron, mercury, copper, and cadmium remain on  
3834 the column.

3835 Numerous paper chromatograph systems employing inorganic or chelating ligands in water or  
3836 organic solvents are available to separate cobalt from other metals. In one system, carrier-free

## Separation Techniques

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3837  $^{60}\text{Co}$  and  $^{59}\text{Fe}$  from an irradiated manganese target were separated with an acetone-hydrochloric  
3838 solvent.

3839 ELECTRODEPOSITION. Most electroanalytical methods for cobalt are preceded by isolating the  
3840 cobalt from interfering ions by precipitation or ion exchange. The electrolyte is usually an  
3841 ammonia solution that produces the hexamine complex of cobalt (II),  $\text{Co}(\text{NH}_3)_6^{+2}$  in solution.  
3842 Reducing agents such as hydrazine sulfate are added to prevent anodic deposits of cobalt and the  
3843 oxidation of the cobalt (II)-amine ion. Cobalt and nickel can be separated electrolytically by  
3844 using an aqueous solution of pyridine with hydrazine to depolarize the platinum anode. The  
3845 nickel is deposited first, and the voltage is increased to deposit cobalt.

### 3846 Methods of Analysis

3847  $^{57}\text{Co}$ ,  $^{58}\text{Co}$ , and  $^{60}\text{Co}$  maybe concentrated from solution by coprecipitation and determined by  
3848 gamma-ray spectrometry.  $^{60}\text{Co}$  is most commonly produced by the neutron activation of  $^{59}\text{Co}$ , in  
3849 a reactor or an accelerator.  $^{58}\text{Co}$  is most commonly produced from the following reaction in  
3850 nuclear reactors,  $^{58}\text{Ni}(\text{n,p})^{58}\text{Co}$ , due to the presence of nickel bearing alloys which undergo  
3851 corrosion and are transported through the reactor core.  $^{58}\text{Co}$  is the most significant contributor to  
3852 the gamma ray induced radiation fields in these facilities.  $^{57}\text{Co}$  can be produced by either of the  
3853 following,  $^{58}\text{Ni}(\text{n,d})^{57}\text{Co}$  [reactor] or  $^{56}\text{Fe}(\text{d,n})^{57}\text{Co}$  [accelerator],  $^{57}\text{Co}$  and  $^{60}\text{Co}$  are frequently  
3854 used as part of a mixed radionuclide source for calibration of gamma ray spectrometers.

3855       Compiled from: Baes and Mesmer, 1976; Bate and Leddicotte, 1961; Cotton and Wilkinson,  
3856       1988; Dale and Banks, 1962; EPA, 1973; Greenwood and Earnshaw, 1984; Haissinsky and  
3857       Adloff, 1965; Hillebrand et al., 1980; Larsen, 1965; Latimer, 1952; Lingane, 1966.

### 3858 14.10.9.4 Iodine

3859 Iodine is a nonmetal, the last naturally occurring member of the halogen series, with an atomic  
3860 number of 53. In the elemental form it is a diatomic molecule,  $\text{I}_2$ , but it commonly exists in one  
3861 of four nonzero oxidation states: -1 with metal ions or hydrogen; and +1, +5, and +7 with other  
3862 nonmetals, often oxygen. Numerous inorganic and organic compounds of iodine exist, exhibiting  
3863 the multiple oxidation states and wide range of physical and chemical properties of the element  
3864 and its compounds. Existence of multiple oxidation states and the relative ease of changing  
3865 between the -1, 0, and +5 state allows readily available methods for separation and purification of  
3866 radionuclides of iodine in radiochemical procedures.

3867 Isotopes

3868 There are 42 known isotopes of iodine, including seven metastable states. The mass numbers  
3869 range from 108 to 142. The only stable isotope is naturally occurring  $^{127}\text{I}$ . The half-lives of the  
3870 radionuclides range from milliseconds to days with the single exception of long-lived  $^{129}\text{I}$   
3871 ( $t_{1/2}=1.57 \times 10^7$  y). Iodine radionuclides with lower mass numbers decay primarily by electron  
3872 capture. The higher mass number are, for the most part, beta emitters. The significant  
3873 radionuclides are  $^{125}\text{I}$  ( $t_{1/2}=60.1\text{d}$ , electron capture),  $^{129}\text{I}$  (beta), and  $^{131}\text{I}$  ( $t_{1/2}=8.0\text{d}$ , beta).

3874 Occurrence and Uses

3875 Iodine is widely distributed, but never found in the elemental form. The average concentration in  
3876 the earth's crust is about 0.3 ppm. In seawater, iodine concentration, in the form of sodium or  
3877 potassium iodide, is low (about 50 ppb), but it is concentrated in certain seaweed, especially kelp.  
3878 It is also found in brackish waters from oil and salt wells. The sources are saltpeter and nitrate-  
3879 bearing earth in the form of calcium iodate, well brine, and seaweed. Iodine is produced from  
3880 calcium iodate by extraction of the iodate from the source with water and reduction of the iodate  
3881 with sodium bisulfite to iodine. Iodine is precipitated by mixing with the original iodate liquor to  
3882 cause precipitation. Iodine can also be obtained from well brine, where the iodide ion is oxidized  
3883 with chlorine, and then the volatile iodine is blown out with a stream of air. Sodium or potassium  
3884 iodide in seaweed is calcined to an ash with sulfuric acid, which oxidizes the iodide to iodine.  
3885 Iodine from any of these processes can be purified by sublimation.

3886 Isotopes of iodine of mass  $\geq 128$  may all be formed as a result of fission of uranium and  
3887 plutonium. Nuclear reactors and bomb tests are the most significant sources of these radioiso-  
3888 topes with the exception of  $^{131}\text{I}$ . That isotope is routinely produced for use in medical imaging  
3889 and diagnosis. The isotopes released from the other sources represent a short term environmental  
3890 health hazard should there be an abnormal release from reactors or if bomb testing or use were to  
3891 occur.

3892 This was the case in both 1979 and 1986 when the power reactor events at Three Mile Island and  
3893 Chernobyl, caused releases of radioiodines. During the former event a ban on milk distribution in  
3894 the downwind corridor was enforced as a purely preventative measure. In the latter case, signifi-  
3895 cant releases of iodines and other isotopes caused more drastic, long term measures for food  
3896 quarantine.

3897 Deposits on the surface of plants could provide a quick source of exposure if consumed directly  
3898 from fruits and vegetables or indirectly from cow's milk. It would readily accumulate in the

3899 thyroid gland, causing a short-term exposure of concern. It represent the greatest short-term  
3900 exposure after a nuclear detonation and has been released in power plant accidents.  $^{129}\text{I}$ , with of a  
3901 half-life of more than 15 million years, represent a long-term environmental hazard. In addition  
3902 to its long half-life, the environmental forms of iodine in the environment are highly soluble in  
3903 groundwater and are poorly sorbed by soil components. It is not absorbed at all by granite, and  
3904 studies at a salt repository indicate that  $^{129}\text{I}$  would be only one of few radionuclides that would  
3905 reach the surface before it decayed. Therefore, research on the fate of  $^{129}\text{I}$  that might be released  
3906 suggests that the radionuclide would be highly disseminated in the ecosystem.

3907  $^{131}\text{I}$  is routinely analyzed for in milk, soil and water.  $^{129}\text{I}$  is a low energy beta and gamma emitter,  
3908 which has a very long half-life ( $1.47 \times 10^7$  years). The most significant concern for this isotope is  
3909 in radioactive waste, and its potential for migration due to the chemistry of iodine in the  
3910 environment.  $^{131}\text{I}$  is produced for medical purposes by neutron reaction as follows:  $^{130}\text{Te}(n,\gamma)^{131}\text{Te}$   
3911  $\rightarrow$  beta decay  $\rightarrow$   $^{131}\text{I}$  (half-life = 8 days).

3912 The major use of iodine, iodine radionuclides, and iodine compounds is in medical diagnosis and  
3913 treatment.  $^{123}\text{I}$ ,  $^{125}\text{I}$ , and  $^{131}\text{I}$  are use for diagnostic imaging of the thyroid gland and the kidneys.  
3914  $^{131}\text{I}$  is used to treat hyperthyroidism and thyroid cancer. Stable iodine in the form of potassium  
3915 iodide is added to commercial salt to prevent enlargement of the thyroid (goiter). Iodine in the  
3916 form of the hormone thyroxine is also used for thyroid and cardiac treatment and hormone  
3917 replacement therapy in iodine deficiency. Iodine radionuclides are used as a tracer in the  
3918 laboratory and industry to study chemistry mechanisms and processes and to study biological  
3919 activity and processes. Iodine is a bactericide and is used as an antiseptic and sterilization of  
3920 drinking water. It is used as a catalyst in chemical processes and as silver iodide in film  
3921 emulsions.

### 3922 Solubility of Compounds

3923 Molecular iodine is only very slightly soluble in water (0.33 g/L), but it is soluble in solutions of  
3924 iodide ion, forming  $\text{I}_3^-$ . It is appreciably soluble in organic solvents. Carbon tetrachloride ( $\text{CCl}_4$ )  
3925 or chloroform ( $\text{CHCl}_3$ ) are commonly used to extract iodine from aqueous solutions after  
3926 alternate forms of the element, typically  $\text{I}^-$  and  $\text{IO}_3^-$ , are converted to  $\text{I}_2$ . The solutions have a  
3927 violet color in organic solvents, and iodine dimerizes to some extent in these solutions:



3929 Numerous compounds of iodine are soluble in water. All metallic iodides are soluble in water  
3930 except those of silver, mercury, lead, cuprous ion, thallium, and palladium. Antimony, bismuth,

3931 and tin iodides require a small amount of acid to keep them in solution. Most of the iodates and  
3932 periodates are insoluble. The iodates of sodium, potassium, rubidium, and the ammonium ion are  
3933 soluble in water. Those of cesium, cobaltous ion, magnesium, strontium, and barium are slightly  
3934 soluble in water but soluble in hot water. Most other metallic iodates are insoluble.

3935 Review of Properties

3936 Elemental iodine ( $I_2$ ) is a purple-black, lustrous solid at room temperature with a density of 4.9  
3937  $g/cm^3$ . The brittle crystals have a slightly metallic appearance. Iodine readily sublimates and stored  
3938 in a closed clear, colorless container, it produces a violet vapor with an irritating odor. Iodine has  
3939 a melting point of 114 °C and a boiling point of 184 °C.

3940 The chemical reactivity of iodine is similar to the other halogens, but it is the least electro-  
3941 negative member of the family of elements and the least reactive. It readily reduces to iodide, and  
3942 is displaced from its iodides by the other halogens and many oxidizing agents. Iodine combines  
3943 directly with most elements to form a large number of ionic and covalent compounds. The  
3944 exceptions are the noble gases, carbon, nitrogen, and some noble metals.

3945 The inorganic compounds of iodine can be classified into three groups: (1) iodides, (2)  
3946 interhalogen, and (3) oxides. Iodine forms iodides that range from ionic compounds such as  
3947 potassium iodide (KI) to covalent compounds such as titanium tetraiodide ( $TiI_4$ ) and phosphorus  
3948 triiodide ( $PI_3$ ), depending on the identity of the combining element. More electropositive (less  
3949 electronegative) metals (on the left side of the periodic table, such as alkali metals and alkaline  
3950 earths) form ionic compounds. Less electropositive metals and more electronegative nonmetals  
3951 tend to form covalent compounds. Interhalogen compounds include the binary halides, such as  
3952 iodine chloride (ICl), iodine trichloride ( $ICl_3$ ), and iodine pentafluoride ( $IF_5$ ), or contain  
3953 interhalogen cations and anions, such as  $ICl_2^{+1}$ ,  $IF_6^{+1}$ ,  $I^{+3}$ ,  $ClIBr^{-1}$ ,  $ICl_4^{-1}$ , and  $I_6^{-2}$ . Oxygen  
3954 compounds constitute the oxides,  $I_2O_5$  and  $I_4O_9$  (containing one  $I^{+3}$  cation and three  $IO_3^{-1}$  anions),  
3955 for example; the oxyacids, such as hypiodous acid (HIO) and iodic acid ( $HIO_3$ ); and compounds  
3956 containing oxyanions, iodates ( $IO_3^{-1}$ ) and periodates ( $IO_4^{-1}$ ) are the common ones.

3957 Organoiodides include two categories: (1) iodides and (2) iodide derivatives with iodine in a  
3958 positive oxidation state because iodine is covalently bonded to another, more electronegative  
3959 element. Organoiodides contain a carbon iodide bond. They are relatively dense and volatile and  
3960 more reactive than the other organohalides. They include the iodoalkanes such as ethyl iodide  
3961 ( $C_2H_5I$ ) and iodobenzene ( $C_6H_5I$ ). Dimethyliodonium (III) hexafluoroantimonate  
3962 [ $(CH_3)_2I^+SbF_6^{-3}$ ], a powerful methylating agent, is an example of the second category.

3963 The toxicity of molecular iodine is primarily related to its vapor state and to solutions. Iodine  
 3964 vapor is an eye and nasal irritant, potentially causing damage to the eyes and serious respiratory  
 3965 damage. Solid iodine is not a serious problem unless confined to the skin where it causes  
 3966 discoloration and eventually burns. Solutions of iodine are toxic if taken internally. The  
 3967 radionuclides of iodine are radiotoxic, primarily because of their concentration in the thyroid  
 3968 gland. Radiotoxicity of  $^{129}\text{I}$ , if released, is a concern because of its extremely long half-life.  $^{131}\text{I}$ ,  
 3969 with a half-life of eight days, is a short-term concern. The whole-body effective biological half-  
 3970 lives of  $^{129}\text{I}$  and  $^{131}\text{I}$  are 140 d and 7.6 d, respectively.

3971 Solution Chemistry

3972 OXIDATION-REDUCTION BEHAVIOR. Iodine can exist in multiple oxidation states in solution, but  
 3973 the radiochemist can control the states by selection of appropriate oxidizing and reducing agents.  
 3974 In acid and alkaline solutions, the common forms of iodine are:  $\text{I}^-$ ,  $\text{I}_2$ , and  $\text{IO}_3^-$ . Hypoiodous acid  
 3975 ( $\text{HIO}$ ) and the hypoiodite ion ( $\text{IO}^-$ ) can form in solution, but they rapidly disproportionate:



3978 Iodine itself is not a powerful oxidizing agent, less than that of the other halogens ( $\text{F}_2$ ,  $\text{Cl}_2$ , and  
 3979  $\text{Br}_2$ ), but its action is generally rapid. Several oxidizing and reducing agents are used to convert  
 3980 iodine into desired oxidation states during radiochemical procedures. These agents are used to  
 3981 promote radiochemical equilibrium between the analyte and the carrier or tracer or to produce a  
 3982 specific oxidation state before separation:  $\text{I}_2$  before extraction in an organic solvent or  $\text{I}^-$  before  
 3983 precipitation, as examples. Table 14.19 presents oxidizing and reducing agents commonly used  
 3984 in radiochemical procedures:

3985 **Table 14.19 — Common radiochemical oxidizing and reducing agents for iodine**

Redox Process	Redox Reagent	Notes
$\text{I}^- \rightarrow \text{I}_2$	$\text{HNO}_2$ ( $\text{NaNO}_2$ in acid)	Does not affect other halides
$\text{I}^- \rightarrow \text{IO}_3^-$	$\text{MnO}_2$ in acid	Well suited for laboratory work
$\text{I}_2 \rightarrow \text{I}^-$	6 M $\text{HNO}_3$ $\text{NaHSO}_3$ and $\text{NaHSO}_4$ (in acid) $\text{Na}_2\text{SO}_3$ and $\text{Na}_2\text{S}_2\text{O}_3$ $\text{Fe}_2(\text{SO}_4)_3$ (in acid)	
$\text{I}^- \rightarrow \text{IO}_4^-$	$\text{KMnO}_4$ 50% $\text{CrO}_3$ in 18N $\text{H}_2\text{SO}_4$	

Redox Process	Redox Reagent	Notes
3991 3992 3993 3994 3995	$I^{-1} \rightarrow IO_4^{-1}$ NaClO in base	
	$IO_4^{-1} \rightarrow I_2$ NH <sub>2</sub> OH·HCl	
	$IO_3^{-1} \rightarrow I_2$ NH <sub>2</sub> OH·HCl H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> in 18N H <sub>2</sub> SO <sub>4</sub>	
	$IO_4^{-1} \rightarrow I^{-1}$ NaHSO <sub>3</sub> in acid	
	$I_2 \rightarrow I^{-1}$ SO <sub>2</sub> gas NaHSO <sub>3</sub> and (NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub>	

3996 Radiochemical exchange between I<sub>2</sub> and I<sup>-1</sup> in solution is complete within time of mixing and  
 3997 before separation. In contrast, exchange between I<sub>2</sub> and IO<sub>3</sub><sup>-1</sup> or IO<sub>4</sub><sup>-1</sup> in acid solution and between  
 3998 IO<sub>3</sub><sup>-1</sup> and IO<sub>4</sub><sup>-1</sup> in acid or alkaline solution is slow. For radiochemical analysis of iodine,  
 3999 experimental evidence indicates that the complete and rapid exchange of radioiodine with carrier  
 4000 iodine can be accomplished by the addition of the latter as I<sup>-1</sup> and subsequent oxidation to IO<sub>4</sub><sup>-1</sup> by  
 4001 NaClO in alkaline solution, addition of IO<sub>4</sub><sup>-1</sup> and reduction to I<sup>-1</sup> with NaHSO<sub>3</sub>, or addition of one  
 4002 followed by redox reactions first to one oxidation state and then back to the original state.

4003 COMPLEXATION. As a nonmetal, iodine is generally not the central atom of a complex, but it can  
 4004 act as a ligand to form complexes such as SiI<sub>6</sub><sup>-2</sup> and CoI<sub>6</sub><sup>-3</sup>. An important characteristic of  
 4005 molecular iodine is its ability to combine with the iodide ion to form polyiodide anions. The  
 4006 brown triiodide is the most stable:



4008 The equilibrium constant for the reaction in aqueous solution at 25 °C is 725, so appreciable  
 4009 concentrations of the anion can exist in solution, and the reaction is responsible for the solubility  
 4010 of iodine in iodide solutions.

4011 HYDROLYSIS. Iodine hydrolyzes in water through a disproportionation reaction:



4013 Because of the low solubility of iodine in water and the small equilibrium constant ( $k=2.0 \times$   
 4014  $10^{-13}$ ), hydrolysis produces negligible amounts of the products ( $6.4 \times 10^{-6}$  M) even when the  
 4015 solution is saturated with iodine. Disproportionation of HIO produces a corresponding minute  
 4016 quantity of IO<sub>3</sub><sup>-1</sup> (see the reaction above). In contrast, in alkaline solution, I<sub>2</sub> produces I<sup>-1</sup> and IO<sup>-1</sup>:



## Separation Techniques

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4018 The equilibrium constant favors the products ( $k=30$ ), but the actual composition of the solution is  
4019 complicated by the disproportionation of  $\text{IO}^{-1}$  (illustrated above), giving  $\text{I}^{-1}$  and  $\text{IO}_3^{-1}$ . The  
4020 equilibrium constant for the reaction of  $\text{IO}^{-1}$  with hydroxide ion is very large ( $10^{20}$ ), and the rate  
4021 of the reaction is very fast at all temperatures. Therefore, the actual products obtained by  
4022 dissolving iodine in an alkaline solution are indeed  $\text{I}^{-1}$  and  $\text{IO}_3^{-1}$ , quantitatively, and  $\text{IO}^{-1}$  does not  
4023 exist in the solution.

### 4024 Dissolution of Samples

4025 Iodine compounds in rocks are often in the form of iodides that are soluble in either water or  
4026 dilute nitric acid when the finely divided ores are treated with one of these agents. Those that are  
4027 insoluble under these conditions are solubilized with alkali fusion with sodium carbonate or  
4028 potassium hydroxide, followed by extraction of the residue with water. Insoluble periodates can  
4029 be decomposed by cautious ignition, converting them to soluble iodides.

4030 Metals containing iodine compounds are dissolved in varying concentrations of nitric, sulfuric, or  
4031 hydrochloric acids. Dissolution can often be accomplished at room temperature or might require  
4032 moderation in an ice bath.

4033 Organoiodides are decomposed with a sodium peroxide, calcium oxide, or potassium hydroxide  
4034 by burning in oxygen in a sealed bomb. Wet oxidation with mixtures of sulfuric and chromic  
4035 acids or with aqueous hydroxide is also used.

### 4036 Separation Methods

4037 PRECIPITATION. The availability of stable iodine as a carrier and the relative ease of producing  
4038 the iodide ion make precipitation a simple method of concentrating and recovering iodine  
4039 radionuclides. The two common precipitating agents are silver ( $\text{Ag}^{+1}$ ) and palladium (II) ( $\text{Pd}^{+2}$ )  
4040 cations, which form silver iodide ( $\text{AgI}$ ) and palladium iodide ( $\text{PdI}_2$ ), respectively. Silver iodide  
4041 can be solubilized with a 30 percent solution of potassium iodide. Palladium precipitates iodide  
4042 in the presence of chloride and bromide, allowing the separation of iodide from these halides.  
4043 The precipitating agent should be free of palladium (IV), which will precipitate chloride. If  
4044 palladium (II) iodide is dried, precaution should be taken as the solid slowly loses iodine if  
4045 heated at  $100\text{ }^\circ\text{C}$ . Iodate can be precipitated as silver iodate, and periodate as lead periodate.

4046 SOLVENT EXTRACTION. One solvent extraction method is commonly used to isolate iodine. After  
4047 preliminary oxidation-reduction steps to insure equilibrium of all iodine in solution, molecular  
4048 iodine ( $\text{I}_2$ ) is extracted from aqueous solutions by a nonpolar solvent, usually carbon tetrachloride

4049 or chloroform. It is not uncommon to add small quantities of the oxidizing or reducing agent to  
4050 the extraction solution to ensure and maintain all iodine in the molecular form. Hydroxylamine is  
4051 added, for example, if iodate is the immediate precursor of iodine before extraction.

4052 ION-EXCHANGE CHROMATOGRAPHY. Both cation and anion exchange procedures are used to  
4053 separate iodine from contaminants. Cation-exchange chromatography has been used to remove  
4054 interfering cations. To remove  $^{137}\text{Cs}$  activity, an iodine sample in the iodide form is absorbed on a  
4055 cation-exchange resin and eluted with ammonium sulfite  $[(\text{NH}_4)_2\text{SO}_3]$ , to ensure maintenance of  
4056 the iodide form. Cesium cations remain the resin. Bulk resin is also used, and iodide is washed  
4057 free of the resin as the periodate with sodium hypochlorite ( $\text{NaClO}$ ) as the oxidizing agent.  
4058 Anion-exchange resins provide absorption of the iodide ion. The halides have been separated  
4059 from each other on an anion-exchange column prepared in the nitrate form by eluting with 1 M  
4060 sodium nitrate. Iodide can also be separated from contaminants by addition to an anion  
4061 exchanger and elution as periodate with sodium hypochlorite. The larger periodate anion is not as  
4062 strongly attracted to the resin as the iodide ion.  $^{131}\text{I}$  separation, collection, and analysis is  
4063 performed by absorbing the radionuclide on an anion-exchange resin and gamma counting it on  
4064 the sealed column after eluting the contaminants.

4065 DISTILLATION. Molecular iodine is a relatively volatile substance. Compared to many  
4066 contaminating substances, particularly metal ions in solution, its boiling point of  $184^\circ\text{C}$  is very  
4067 low, and the volatility of iodine provides a method for its separation from other substances. After  
4068 appropriate oxidation-reductions steps to convert all forms of iodine into the molecular form,  
4069 iodine is distilled from aqueous solution into sodium hydroxide and collected by another  
4070 separation process, typically solvent extraction. In hydroxide solution, molecular iodine is  
4071 converted to a mixture of iodide and hypoiodite ions and then into iodide and periodate ions, and  
4072 suitable treatment is required to convert all forms into a single species for additional procedures.

#### 4073 Methods of Analysis

4074 Macroquantities of iodine can be determined gravimetrically by precipitation as silver iodide or  
4075 palladium iodide. The latter substance is often used to determine the chemical recovery in  
4076 radiochemical analyses. Microquantities of  $^{129}\text{I}$  and  $^{131}\text{I}$  are coprecipitated with palladium iodide  
4077 using stable iodide as a carrier and counted for quantification.  $^{129}\text{I}$  usually is beta counted in a  
4078 liquid-scintillation system, but it can also be determined by gamma-ray spectrometry.  $^{131}\text{I}$  is  
4079 determined by gamma-ray emission.

4080 Compiled from: Adams, 1995; APHA, 1998; Armstrong et al., 1961; Bailar et al., 1984;  
4081 Choppin et al., 1995; Considine and Considine, 1983; Cotton and Wilkinson, 1988; DOE,

4082 1990 and 1997, 1997; EPA, 1973; EPA, 1980; Ehmann and Vance, 1991; Greenwood and  
4083 Earnshaw, 1984; Haissinsky and Adloff, 1965; Kleinberg and Cowan, 1960; Latimer, 1952;  
4084 Lindsay, 1988.

#### 4085 14.10.9.5 Plutonium

4086 Plutonium, with an atomic number of 94 is an actinide and the second element in the transuranic  
4087 series. Essentially all plutonium is an artifact, most produced by neutron bombardment of  $^{238}\text{U}$   
4088 followed by two sequential beta emissions, but trace quantities of plutonium compounds can be  
4089 found in the natural environment. Plutonium radiochemistry is complicated by the five possible  
4090 oxidation states that can exist; four can be present in solution at one time.

#### 4091 Isotopes

4092 Plutonium has 18 isotopes with mass numbers ranging from 232 to 247, and all isotopes are  
4093 radioactive. Some have a long half-life: the isotope of greatest importance,  $^{239}\text{Pu}$ , has a half-life  
4094 of 24,110 years, but  $^{242}\text{Pu}$  and  $^{244}\text{Pu}$  have a half-lives of 376,000 and 76,000,000 years,  
4095 respectively.  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{241}\text{Pu}$  have a half-lives of 87.74, 6,537, and 14.4 years, respectively.  
4096 Four of these isotopes decay by alpha emission accompanied by weak gamma rays:  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  
4097  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$ . In contrast,  $^{241}\text{Pu}$  decays by beta emission with weak gamma rays but its progeny  
4098 is  $^{241}\text{Am}$ , an intense gamma emitter.  $^{239}\text{Pu}$  and  $^{241}\text{Pu}$  are fissile materials—they can be split by  
4099 both fast and slow neutrons.  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$  are fissionable but have very small neutron fission  
4100 cross-sections.  $^{240}\text{Pu}$  partly decays by spontaneous fission, although a small amount of  
4101 spontaneous fission occurs in most plutonium isotopes.

#### 4102 Occurrence and Uses

4103 There are minute quantities of plutonium compounds in the natural environment as the result of  
4104 thermal neutron capture and subsequent beta decay of naturally occurring  $^{238}\text{U}$ . All plutonium of  
4105 concern is an artifact, the result of neutron bombardment of uranium in a nuclear reactor.  
4106 Virtually all nuclear power-plants of all sizes and the waste from the plants contain plutonium  
4107 because  $^{238}\text{U}$  is the main component of fuel used in nuclear reactors. It is also associated with the  
4108 nuclear weapons industry and its waste. Virtually all the plutonium in environmental samples is  
4109 found in air samples as the results of atmospheric weapons testing. Plutonium in plant and crop  
4110 samples is essentially caused by surface absorption.

4111 Plutonium is produced in nuclear reactors from  $^{238}\text{U}$  that absorbs neutrons emitted by the fission  
4112 of  $^{235}\text{U}$ , which is a naturally occurring uranium isotope found with  $^{238}\text{U}$ .  $^{239}\text{U}$  is formed and emits

4113 a beta particle to form  $^{239}\text{Np}$  that decays by beta emission to form  $^{239}\text{Pu}$ . Once started, the process  
4114 is spontaneous until the uranium fuel rods become a specific uranium-plutonium mixture. The  
4115 rods are dissolved in acid, and plutonium is separated primarily by solvent extraction, finally  
4116 producing a concentrated plutonium solution. Pure plutonium metal can be prepared by  
4117 precipitating plutonium peroxide or oxalate, igniting the precipitate to  $\text{PuO}_2$ , converting the oxide  
4118 to  $\text{PuF}_3$ , and reducing Pu(III) to the metal in an ignited mixture containing metallic calcium.

4119 Large quantities of  $^{239}\text{Pu}$  have been used as the fissile agent in nuclear weapons and as a reactor  
4120 fuel when mixed with uranium. It is also used to produce radioactive isotopes for research,  
4121 including the study of breeder reactors, and  $^{238}\text{Pu}$  is used as a heat source to power instruments  
4122 for space exploration and implanted heart pacemakers.

### 4123 Solubility of Compounds

4124 General solubility characteristics include the insolubility of the hydroxides, fluorides, iodates,  
4125 phosphates, carbonates, and oxalates of Pu(III) and Pu(IV). Some of these can be dissolved in  
4126 acid solution, however. The corresponding compounds of  $\text{PuO}_2^{+1}$  and  $\text{PuO}_2^{+2}$  are soluble, with the  
4127 exception of the hydroxides. The binary compounds represented by the carbides, silicides,  
4128 sulfides, and selenides are of particular interest because of their refractory nature. One of the  
4129 complicating factors of plutonium chemistry is the formation of a polymeric material by  
4130 hydrolysis in dilute acid or neutral solutions. The polymeric material can be a complicating factor  
4131 in radiochemical procedures and be quite unyielding in attempts to destroy it.

### 4132 Review of Properties

4133 Plutonium metal has some unique physical properties: a large piece is warm to the touch because  
4134 of the energy produced by alpha decay, and it exists in six allotropic forms below its melting  
4135 point at atmospheric pressure. Each form has unusual thermal expansion characteristics that  
4136 prevents the use of unalloyed plutonium metal as a reactor fuel. The delta phase, however, can be  
4137 stabilized by the addition of aluminum or gallium and be used in reactors. Chemically, plutonium  
4138 can exist in five oxidation states: III, IV, V, VI, and VII. The first four states can be observed in  
4139 solution, and solid compounds of all five states have been prepared. The metal is a silver-grey  
4140 solid that tarnishes in air to form a yellow oxide coating. It is chemically reactive combining  
4141 directly with the halogens, carbon, nitrogen, and silicon.

4142 Plutonium is a very toxic substance, but outside the body, it does not represent great danger from  
4143 its low penetrating alpha emission or emission of its low intensity beta, gamma, or neutron  
4144 radiation. Ingested plutonium is not readily absorbed into the body, but passes through the

4145 digestive tract and expelled before it can cause significant harm. Inhaled plutonium presents a  
4146 significant danger. Particularly, inhalation of particles smaller than one micron would be a  
4147 serious threat due to the alpha-emitting radionuclide being in direct contact with lung tissue.  
4148 Plutonium would also be very dangerous if it were to enter the blood stream through an open  
4149 wound, because it would concentrate in the liver and bones, leading to damage to the bone  
4150 marrow and subsequent related problems. For these reasons, plutonium is handled in gloveboxes  
4151 with associated precautions taken to protect the worker from direct contact with the material.  
4152 When working with plutonium in any form, precautions should also be taken to prevent the  
4153 accumulation of quantities of fissionable plutonium that would achieve a critical mass,  
4154 particularly in solution where it is more likely to become critical than solid plutonium.

4155 Most of the plutonium in the environment is the result of weapons testing. More than 99 percent  
4156 of the plutonium from these activities was released during atmospheric tests, but a small portion  
4157 was also released during ground tests. An even smaller quantity is released by nuclear fuel  
4158 reprocessing plants, some in the ocean, and by nuclear waste repositories. Part of the atmospheric  
4159 plutonium, originally part of the weapons, settled to the earth as an insoluble oxide, locating in  
4160 the bottom sediments of lakes, rivers, and oceans or becoming incorporated in sub-surface soils.  
4161 The majority of environmental plutonium isotopes are the result of atmospheric nuclear bomb  
4162 tests. If the bomb material is made from uranium, the oxide is enriched to high percentages of  
4163  $^{235}\text{U}$ , the fissile isotope. The  $^{238}\text{U}$  isotope does not fission, but absorbs 1-2 neutrons during the  
4164 explosion forming isotopes of  $^{239}\text{U}$  and  $^{240}\text{U}$ . These isotopes beta decay within hours to their  
4165 neptunium progeny, which in turn decay to  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . Bombs from plutonium would yield  
4166 higher fractions of  $^{240,241,242}\text{Pu}$ .

4167 Plutonium formed as a result of atmospheric tests is most likely to be in the form of a fine  
4168 particulate oxide. If as in the case of a low altitude or underground test, there is a soil component,  
4169 the plutonium will be fused with siliceous minerals. The behavior of the soluble form of  
4170 plutonium would be similar to that released from fuel reprocessing plants and from nuclear waste  
4171 sites. Like the insoluble oxide, most of the soluble form is found in sediments and soils, but a  
4172 small percentage is associated with suspended particles in water. Both the soluble form of  
4173 plutonium and the form suspended on particulate matter are responsible for plutonium transporta-  
4174 tion in the environment. Plutonium in soil is found where the humic acid content is high. In non-  
4175 humic, carbonate-rich soils, plutonium migrates downward. Migration in the former soil is slow  
4176 ( $\leq 0.1$  cm/y) and in the latter it is relatively fast (1-10 cm/y). In subsurface oxic soil, plutonium is  
4177 relatively mobile, transported primarily by colloids. In wet anoxic soils, most of the plutonium is  
4178 quickly immobilized, although a small fraction remains mobile. The average time plutonium  
4179 remains in water is proportional to the amount of suspended material. For this reason, more than

4180 90 percent of plutonium is removed from costal water, while the residence time in mid-ocean  
 4181 water where particulate matter is less is much longer.

4182 Solution Chemistry

4183 The equilibration problems of plutonium are among the most complex encountered in  
 4184 radiochemistry. Plutonium can form five oxidation states in solution, +3, +4, +5, +6, and +7. The  
 4185 first four are present in solution as  $\text{Pu}^{+3}$ ,  $\text{Pu}^{+4}$ ,  $\text{PuO}_2^{+1}$ ,  $\text{PuO}_2^{+2}$ . They coexist in dilute acid  
 4186 solution, and sometimes all four are present in substantial quantities. Problems of disproportiona-  
 4187 tion and auto-oxidation in freshly prepared solutions also complicate the chemistry of plutonium.  
 4188 The +7 state can form in alkaline solutions, and it has been suggested that the ion in solution is  
 4189  $\text{PuO}_5^{-3}$ . Plutonium ions tend to hydrolyze and form complex ions in solution. The +4 ion can  
 4190 form long chain polymers that do not exhibit the usual chemical behavior of the +4 oxidation  
 4191 state. Finally, the different oxidation states exhibit radically different chemical behavior. As a  
 4192 result of these effects, it is possible to mix a plutonium sample with plutonium tracer, subject the  
 4193 mixture to a relatively severe chemical treatment using hot acids or similar reagents, and still  
 4194 selectively recover portions of either the tracer or the sample. This characteristic explains the  
 4195 challenge in achieving reproducible radiochemical results for plutonium.

4196 OXIDATION-REDUCTION BEHAVIOR. Numerous redox agents are available to oxidize and reduce  
 4197 any of the five states of plutonium to alternate oxidation states. The following table provides a  
 4198 convenient method of preparation of each state and illustrates the use of redox reagents in  
 4199 plutonium chemistry:

**Table 14.20 — Redox agents in plutonium chemistry**

Oxidation State	Form	Method of Preparation
III	$\text{Pu}^{+3}$	Dissolve Pu metal in HCl and reduce $\text{Pu}^{+4}$ with $\text{NH}_2\text{OH}$ , $\text{N}_2\text{H}_4$ , $\text{SO}_2$ , or by cathodic reduction
IV	$\text{Pu}^{+4}$	Oxidize $\text{Pu}^{+3}$ with hot $\text{HNO}_3$ ; treat $\text{Pu}^{+3}$ or $\text{PuO}_2^{+2}$ with $\text{NO}_2^{-1}$
IV	$\text{PuO}_2 \cdot n\text{H}_2\text{O}$ (polymer)	Heat $\text{Pu}^{+4}$ in very dilute acid; peptize $\text{Pu}(\text{OH})_4$
V	$\text{PuO}_2^{+1}$	Reduce $\text{PuO}_2^{+2}$ with stoichiometric amount of $\text{I}^{-1}$ or ascorbic acid; electrolytic reduction of $\text{PuO}_2^{+2}$
VI	$\text{PuO}_2^{+2}$	Oxidize $\text{Pu}^{+4}$ with hot dilute $\text{HNO}_3$ or $\text{AgO}$ ; ozonize $\text{Pu}^{+4}$ in cold dilute $\text{HNO}_3$ with $\text{Ce}^{+3}$ or $\text{Ag}^{+1}$ catalyst
VII	$\text{PuO}_5^{-3}$ (?)	Oxidize $\text{PuO}_2^{+2}$ in alkali with $\text{O}_3$ , $\text{S}_2\text{O}_8^{-2}$ or radiation

4208 Unlike uranium, the +3 oxidation state is stable enough in solution to be useful in separation  
4209 chemistry. Disproportionation reactions convert  $\text{Pu}^{+4}$  to  $\text{Pu}^{+3}$  and  $\text{PuO}_2^{+2}$  releasing  $\text{H}^{+1}$ . The  
4210 presence of acid in the solution or complexing agents represses the process. Similarly,  $\text{PuO}_2^{+1}$   
4211 disproportionates producing the same products but with the consumption of  $\text{H}^{+1}$ . For this reason,  
4212  $\text{PuO}_2^{+1}$  is not predominant in acid solutions. These disproportionation reactions can be involved  
4213 in redox reactions by other reagents. Instead of direct oxidation or reduction, the disproportiona-  
4214 tion reaction can occur first, followed by direct oxidation or reduction of one of the products.

4215 It is possible to prepare stable aqueous solutions in which appreciable concentrations of the first  
4216 four oxidation states exist simultaneously: the +3, +4, +5, and +6 states. The relative proportions  
4217 of the different oxidation states depend on the acid, the acid concentration, the method of  
4218 preparation of the solution, and the initial concentrations of each of the oxidation states. These  
4219 relative concentrations will change over time and ultimately establish an equilibrium specific to  
4220 the solution. In 0.5 M HCl at 25 °C, for example, the equilibrium percentages of the four  
4221 oxidation states prepared from initially pure  $\text{Pu}^{+4}$  are +3 (27.2%), +4 (58.4%), +5 (0.7%), and +6  
4222 (13.6%). Freshly prepared plutonium samples are frequently in the +4 state, while an appreciable  
4223 amount of the +3 and +6 oxidation states will be present in long-standing tracer solutions.

4224 A convenient solution to this plutonium equilibration problem takes the form of a two step  
4225 process:

- 4226 • boil the combined sample and tracer with a concentrated inorganic acid (e.g.,  $\text{HNO}_3$ ) to  
4227 destroy any +4 polymers that might have formed, and
- 4228 • cool and dilute the solution; then rapidly (to avoid reforming polymers) treat the solution  
4229 with excess iodide ion (solution turns brown or black) to momentarily reduce all of the  
4230 plutonium to the +3 oxidation state.

4231 The solution will immediately start to disproportionate in the acid medium, but the plutonium  
4232 will have achieved a true equilibrium starting at a certain time from one state in the solution.

4233 Alpha particles emitted by  $^{239}\text{Pu}$  can decompose solutions of the radionuclide by radiolysis. The  
4234 radiolysis products then oxidize or reduce the plutonium, depending on the nature of the solution  
4235 and the oxidation state of the element. The nature of the anion present greatly influences the rate  
4236 of the redox process. For the radiochemist it is important to recognize that for old plutonium  
4237 solutions, particularly those in low acidity, the oxidation labeled states are not reliable.

4238 HYDROLYSIS AND POLYMERIZATION. Hydrolysis is most pronounced for relatively small and  
4239 highly charged ions such as  $\text{Pu}^{+4}$ , but plutonium ions in any oxidation state are more easily  
4240 hydrolyzed than their larger neptunium and uranium analogues.

4241 Trivalent plutonium tends to hydrolyze more than neptunium or uranium, but the study of its  
4242 hydrolysis characteristics has been hindered by precipitation, formation of  $\text{Pu}^{+4}$ , and unknown  
4243 polymerization. In strongly alkaline solutions,  $\text{Pu}(\text{OH})_3$  precipitates; the solubility product  
4244 constant is estimated to be  $2 \times 10^{-20}$ .

4245 Plutonium(IV) exists as a hydrated ion in solutions that are more acidic than  $0.3 \text{ M H}^{+1}$ . Below  
4246  $0.3 \text{ M}$ , it undergoes much more extensive hydrolysis than any other plutonium species, or at  
4247 lower acidities ( $0.1 \text{ M}$ ) if the plutonium concentration is lower. Thus, the start of hydrolysis  
4248 depends on the acid/plutonium ratio as well as the temperature and presence of other ions. On  
4249 hydrolysis, only  $\text{Pu}(\text{OH})^{+3}$  is important in the initial phases, but it tends to undergo irreversible  
4250 polymerization, forming polymers with molecular weights as high as  $10^{10}$  and chemical  
4251 properties much different from the free ion. Presence of the polymer can be detected by its bright  
4252 green color. When plutonium (IV) hydroxide [ $\text{Pu}(\text{OH})_4$ ] is dissolved in dilute acid, the polymer  
4253 also forms. Similarly, if a solution of  $\text{Pu}^{+4}$  in moderately concentrated acid is poured slowly into  
4254 boiling water, extensive polymerization occurs. The colloidal character of the polymer is  
4255 manifested by its strong adsorption onto glass, silica, or small bits of paper or dirt. The chemical  
4256 characteristics of the polymer, with regard to precipitation, ion-exchange, and solvent extraction,  
4257 is markedly different than the chemistry of the common +4 oxidation state of plutonium. Care  
4258 should be taken in the laboratory to avoid the formation of these polymers. For instance, these  
4259 polymers can be formed by overheating solutions during evaporation. Moreover, diluting an  
4260 acidic plutonium solution with water can cause polymerization because of localized areas of low  
4261 acidity, even when the final concentration of the solution is too high for polymerization.  
4262 Therefore, plutonium solutions should always be diluted with acid rather than water. Polymeric  
4263 plutonium can also be formed if insufficient acid is used when dissolving plutonium (IV)  
4264 hydroxide.

4265 Immediately after formation, these polymers are easy to decompose by acidification with  
4266 practically any concentrated inorganic acid or by oxidation. Because depolymerization is slow at  
4267 room temperature and moderate acid concentrations, solutions should be made at least  $6 \text{ M}$  and  
4268 boiled to destroy the polymers. The polymer is rapidly destroyed under these conditions. Adding  
4269 strong complexing agents such as fluoride, sulfate, or other strong complexing agents can  
4270 increase the rate of depolymerization. However, if the polymers are allowed to "age," they can be  
4271 very difficult to destroy.

## Separation Techniques

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4272 The  $\text{PuO}_2^{+1}$  ion has only a slight tendency to hydrolyze, beginning at pH 8, but study of the extent  
4273 of the process is inhibited by the rapid disproportionation of hydrolyzed plutonium(V).

4274 Hydrolysis of  $\text{PuO}_2^{+2}$  is far more extensive than expected for a large +2 ion. Hydrolysis begins at  
4275 pH of about 2.7 to 3.3, giving an orange color to the solution that yields to bright yellow by pH 5.  
4276 Between pH 5 and 7, dimerizations seem to occur, and by pH 13 several forms of plutonium  
4277 hydroxide have been precipitated with solubility products of approximately  $2.5 \times 10^{-25}$ .

4278 COMPLEXATION. Plutonium ions tend to form complex ions in the following order:



4280 Divalent anions tend to form stronger complexes, and the order for simple anions with  $\text{Pu}^{+4}$  is:

4281 carbonate > oxalate > sulfate > fluoride > nitrate >  
4282 chloride > bromide > iodide > perchlorate

4283 Complexation is preferably through oxygen and fluorine rather than nitrogen, phosphorus, or  
4284 sulfur. Plutonium also forms complexes with ligands such as phosphate, acetate, and  
4285 tributylphosphate (TBP). Strong chelate complexes form with EDTA, tartrate, citrate, 2-  
4286 thenoyltrifluoroacetone (TTA), acetylacetone (acac), and cupferron. Plutonium(IV) forms a  
4287 strong complex with fluoride ( $\text{PuF}^{+3}$ ) that is used to solubilize plutonium oxides and keep it in  
4288 the aqueous phase during extraction of other elements with organic solvents. The complex with  
4289 nitrate,  $\text{Pu}(\text{NO}_3)_6^{-2}$ , allows the recovery of plutonium from nuclear fuels. Carbonate and acetate  
4290 complexes prevent precipitation of plutonium from solution even at relatively high pH.

### 4291 Dissolution of Samples

4292 Metallic plutonium dissolves in halogen acids such as hydrochloric acid, but not in nitric or  
4293 concentrated sulfuric acids. The metal dissolves in hydrofluoric nitric acid mixtures. Plutonium  
4294 oxide dissolves with great difficulty in usual acids when ignited. Boiling with concentrated nitric  
4295 acid containing low concentrations of hydrofluoric acid or with concentrated phosphoric acid is  
4296 used. Fusion methods have also been used to dissolve the oxide as well as other compounds of  
4297 plutonium. Plutonium in biological samples is readily soluble, in the case of metabolized  
4298 plutonium in excreted samples, or highly refractory, in the case of fallout samples. Most  
4299 procedures for fallout or environmental samples involve treatment with hydrofluoric acid or  
4300 fusion treatment with a base.

4301 Separation Methods

4302 Extensive work has been done on methods to separate plutonium from other elements. Both  
4303 laboratory and industrial procedures has received considerable treatment. The methods described  
4304 below represents only a brief approach to separation of plutonium, but they indicate the nature of  
4305 the chemistry employed.

4306 PRECIPITATION AND COPRECIPITATION. Macro quantities of plutonium are readily precipitated  
4307 from aqueous solution, and the methods is the basis of separating plutonium from other  
4308 radionuclides in some procedures. Contamination of other metals can be a problem, however;  
4309 zirconium and ruthenium give the most trouble. Plutonium is precipitated primarily as the  
4310 hydroxide, fluoride, peroxide, or oxalate. Both Pu(III) and Pu(IV) are precipitated from acid  
4311 solution by potassium or ammonium hydroxide as hydrated hydroxides or hydrous oxides. On  
4312 redissolving in acid, Pu (IV) tends to form the polymer, and high concentration of acid is needed  
4313 to prevent its formation. Pu(IV) peroxide is formed on the addition of hydrogen peroxide to  
4314 Pu(III), Pu(IV), Pu(V), and Pu(VI) because of the oxidizing nature of hydrogen peroxide. The  
4315 procedure has been used to prepare highly pure plutonium compounds from americium and  
4316 uranium.

4317 Coprecipitation of plutonium can be very specific with the control of its oxidation states and  
4318 selection of coprecipitating reagents. Lanthanum fluoride, a classical procedure for coprecipita-  
4319 tion of plutonium, will bring down Pu(III) and Pu(IV) but not Pu(VI). Only elements with similar  
4320 redox and coprecipitation behavior interfere. Separation from other elements as well as  
4321 concentration from large volumes with lanthanum fluoride is also important because not many  
4322 elements form acid-soluble lanthanum fluoride coprecipitates. Bismuth phosphate ( $\text{BiPO}_4$ ) is also  
4323 used to coprecipitate Pu(III) and Pu(IV). In contrast to lanthanum fluoride and bismuth  
4324 phosphate, zirconium phosphate ( $\text{ZrPO}_4$ ) and an organic coprecipitate, zirconium phenylarsenate  
4325 [ $\text{Zr}(\text{C}_6\text{H}_5)_3\text{AsO}_4$ ], will coprecipitate Pu(IV) exclusively.

4326 SOLVENT EXTRACTION. A wide variety of organic extractants have been developed to separate  
4327 plutonium from other radionuclides and metals by selectively extracting them from aqueous  
4328 media. The extractants, among others, include organophosphorus compounds such as phosphates  
4329 (organoesters of phosphoric acid), amines and their quaternary salts, alcohols, ketones, ethers,  
4330 and amides. Chelating agents such as thenoyltrifluoroacetone (TTA) and cupferron have also  
4331 been used. Numerous studies have been performed on the behavior of these systems. It has been  
4332 found that the performance of an extracting system is primarily related to the organic solvent in  
4333 which the extractant is dissolved and the concentration of the extractant in the solvent, the nature  
4334 of the aqueous medium (the acid present and its concentration (pH) and the presence of salting

4335 agents), the temperature of the system, and the presence and nature of oxidizing agents. One  
4336 common system, used extensively in the laboratory and in industrial process to extract plutonium  
4337 from fission products, illustrates the use of solvent extraction to separate plutonium from  
4338 uranium and other metals. The PUREX process (plutonium uranium reduction extraction) is used  
4339 in most fuel reprocessing plants to separate the radionuclides. It employs TBP, tri-*n*-butyl  
4340 phosphate [(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>PO], in a hydrocarbon solvent, as the extractant. The uranium fuel is dissolved  
4341 in nitric acid as Pu(III), and plutonium is oxidized to Pu(IV) and uranium to U(VI) by oxidizing  
4342 agents. Plutonium and uranium are extracted into a 30 percent TBP solution, and the organic  
4343 phase is scrubbed with nitric acid solution to remove impurities. The plutonium is removed by  
4344 back-extracting it as Pu(III) with a nitric acid solution containing a reducing agent.

4345 Solvent extraction chromatography has provided an efficient, easy technique for rapidly  
4346 separating plutonium and other transuranic elements. A process using octylphenyl-N,N-  
4347 diisobutyl carbamoylphosphine oxide (CMPO) in TBP and fixed on an inert polymeric resin  
4348 matrix has been used to isolate plutonium (IV). All plutonium in the analyte is adjusted to  
4349 plutonium (IV), and the column is loaded from 2 M nitric acid. Plutonium is eluted with 4 M  
4350 hydrochloric acid and 0.1 M hydroquinone or 0.1 M ammonium hydrogen oxalate (NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub>).  
4351 It is important to note that iron, found in most environmental samples, does not effect the  
4352 separation if the element is kept in the +2 oxidation state as ferrous ions. This is commonly  
4353 achieved using ascorbic acid. The ferric ion (Fe<sup>+3</sup>) is detrimental to the separation.

4354 ION-EXCHANGE CHROMATOGRAPHY. Ion-exchange chromatography has been used extensively  
4355 for the radiochemical separation of plutonium. All cationic plutonium species in non-complexing  
4356 acid solutions readily exchanges onto cation resins at low acid concentrations and desorb at high  
4357 acid concentrations. Plutonium in all its oxidation states form neutral or anionic complexes with  
4358 various anions, providing an alternate means for eluting the element. Various cation-exchange  
4359 resins have been used with hydrochloric, nitric, perchloric, and sulfuric acids for separation of  
4360 plutonium from metals including other actinides, but the most common use of plutonium cation-  
4361 exchange chromatography is concentrating a dilute solution or separation from nonabsorbable  
4362 impurities such as organic reagents, redox agents, for example.

4363 Anion-exchange chromatography is the primary ion-exchange method for the separation of  
4364 plutonium from other metals and the separation of the plutonium oxidation states, and many  
4365 procedures have been developed using this method. On a strong anion-exchange resin, for  
4366 example, the higher oxidation states (IV, V, and VI) occurs at hydrochloric acid concentrations  
4367 above 6 M, while desorption occurs at 2 M acid. Plutonium (III) does not absorb on the column,  
4368 and plutonium (VI) absorbs from 2 to 3 M hydrochloric acid solution. Plutonium can be  
4369 separated from other actinides and most other elements by absorbing the plutonium cations—

4370 Pu(IV) and Pu (VI)—onto a strong-anion resin from 6 M hydrochloric acid, and subsequently  
4371 eluting the plutonium by reducing it to plutonium III. Anion exchange in 7 to 8 M nitric acid is  
4372 also an effective method for separating plutonium. The radionuclide loads on the column as  
4373  $\text{Pu}(\text{NO}_3)_6^{-2}$  and is eluted with dilute acid or after reduction.

4374 ELECTRODEPOSITION. Separation methods based on electrodeposition are not common, but one  
4375 method for the alpha analysis of plutonium is in use. Plutonium is electrodeposited on a stainless  
4376 steel disc from an ammonium sulfate solution at 1.2 amps for one hour. The separation is used  
4377 after isolating the radionuclide by extraction chromatography, and the plutonium isotopes are  
4378 resolved by alpha spectroscopy.

#### 4379 Methods of Analysis

4380  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{241}\text{Pu}$  are collected for analysis either by electrodeposition on a platinum or  
4381 nickel disc or by microprecipitation with lanthanum fluoride ( $\text{LaF}_3$ ). Radionuclides of  $^{238}\text{Pu}$ ,  
4382  $^{239}\text{Pu}$ , and  $^{240}\text{Pu}$  are determined by alpha spectrometry or gas flow proportional counting.  $^{241}\text{Pu}$  is  
4383 beta counted.  $^{236}\text{Pu}$  or  $^{242}\text{Pu}$  are used as a tracer for measuring chemical yield. They are measured  
4384 by alpha spectrometry.

4385 Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Coleman, 1965; Cotton and  
4386 Wilkinson, 1988; DOE 1990, 1995, and 1997; EPA 1973 and 1980; Metz and Waterbury,  
4387 1962; Seaborg and Loveland, 1990; Weigel et al., 1986.

#### 4388 14.10.9.6 Radium

4389 Radium, with an atomic number of 88, is the heaviest (last) member of the family of alkaline  
4390 earth metals, which, in addition, includes beryllium (Be), magnesium (Mg), calcium (Ca),  
4391 strontium (Sr), and barium (Ba). It is the most basic and reactive of the series, and exists  
4392 exclusively as +2 cations in compounds and solution. All isotopes are radioactive, and essentially  
4393 all analyses are made by radioactive measurements.

#### 4394 Isotopes

4395 There are 25 isotopes of radium from  $^{205}\text{Ra}$  to  $^{234}\text{Ra}$ ; all are radioactive. The most important with  
4396 respect to the environmental contamination are members of the  $^{238}\text{U}$  and  $^{232}\text{Th}$  naturally occurring  
4397 decay series:  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , respectively.  $^{226}\text{Ra}$  is the most abundant isotopic form with a half-  
4398 life of 1,602 years. As a member of the  $^{238}\text{U}$  series, it is produced by alpha emission from  $^{230}\text{Th}$ .  
4399  $^{226}\text{Ra}$  emits an alpha particle and, in turn, produces  $^{222}\text{Rn}$ , an inert gas that is also an alpha

4400 emitter. Radium generates radon at the rate of 0.1  $\mu\text{L}$  per day per gram of radium, and its  
4401 radioactivity decreases at the rate of about one percent each 25 years.  $^{228}\text{Ra}$ , half-life of 5.77  
4402 years, is produced in the  $^{232}\text{Th}$  decay series by emission of an alpha particle from  $^{232}\text{Th}$  itself.

4403 Occurrence

4404 In nature, radium is primarily associated with uranium and thorium, particularly in the uranium  
4405 ores—carnotite and pitchblende, where  $^{226}\text{Ra}$  is in radioactive equilibrium with  $^{238}\text{U}$  and its other  
4406 progeny. The widespread dispersal of uranium in rocks and minerals results in a considerable  
4407 distribution of radium isotopes throughout nature. It is generally found in trace amounts in most  
4408 materials, therefore, the radium/uranium ratio is about 1 mg radium per 3 kg uranium (1 part in 3  
4409  $\times 10^6$  parts uranium). This leads to a terrestrial abundance of approximately  $10^{-6}$  ppm:  $10^{-12}\text{g/g}$  in  
4410 rocks and minerals. Building materials, such as bricks and concrete blocks for example, that  
4411 contain mineral products also contain radium. With leaching from soil, the concentration is about  
4412  $10^{-13}\text{g/L}$  in river and streams, and uptake in biological systems produces concentrations of  
4413  $10^{-14}\text{g/g}$  in plants and  $10^{-15}\text{g/g}$  in animals.

4414 Uranium ores have been processed with hot mineral acids or boiling alkali carbonate to remove  
4415 radium and/or uranium. Extracted radium was usually coprecipitated with barium sulfate,  
4416 converted to carbonate or sulfide, and solubilized with hydrochloric acid. Separation from  
4417 barium was usually accomplished by fractional crystallization of the chlorides, bromides, or  
4418 hydroxides, since barium salts are usually slightly more soluble. The free metal has been  
4419 prepared by electrolysis of radium chloride solutions, using a mercury cathode. The resulting  
4420 amalgam is thermally decomposed in a hydrogen atmosphere to produce the pure metal. The  
4421 waste streams from these industrial operations contain radium, primarily as a coprecipitate of  
4422 barium sulfate. Since many other natural ores also contain uranium and radium, processing can  
4423 result in uranium and its equilibrium progeny appearing in a product or byproduct. Apatite, a  
4424 phosphate ore, is used to produce phosphoric acid, and the gypsum byproduct contains all the  
4425 radium originally present in the ore.

4426  $^{226}\text{Ra}$  extracted from ores has historically been used in diverse ways as a source of radioactivity.  
4427 It has been mixed with a scintillator to produce luminous paint, and at one time, the most  
4428 common use for its salts was radiation therapy. As a source of gamma radiation, radium activity  
4429 was enhanced by sealing a radium salt in a capsule that prevented escape of the gaseous progeny,  
4430  $^{222}\text{Rn}$ , and allowing the radon to decay into its successive progeny. Two progeny are  $^{214}\text{Pb}$  and  
4431  $^{214}\text{Bi}$ , the principal emitters of gamma radiation in the source. For the most part radium has been  
4432 replaced in medical technology by other sources of radioactivity, but numerous capsules  
4433 containing the dry, concentrated substances still exist.

4434 Radium salts are used in various instruments for inspecting structures such as metal castings by  
4435 gamma-ray radiography, to measure the thickness of catalyst beds in petroleum cracking units,  
4436 and to continuously measure and control the thickness of metals in rolling mills. Radium is also  
4437 used for the preparation of standard sources of radiation, as a source of actinium and protac-  
4438 tinium, and as a source of ionizing radiation in static charge eliminators. In combination with  
4439 beryllium, it is a neutron source for research, in the analysis of materials by neutron activation,  
4440 and radio-logging of oil wells.

4441 Radium in the environment is the result of natural equilibration and anthropological activity such  
4442 as mining and processing operations. Radium is retained by many rock and soil minerals,  
4443 particularly clay minerals, and migrates only very slowly in through these materials. The decay  
4444 progeny of  $^{226}\text{Ra}$ , gaseous  $^{222}\text{Rn}$ , is an important environmental pollutant and represents the most  
4445 significant hazard from naturally occurring radium. Concentration of the alpha-emitting gas in  
4446 some occupied structures contributes to the incidence of lung cancer in humans. During the  
4447 decay of  $^{226}\text{Ra}$ , the recoil of the parent nucleus after it emits an alpha particle, now  $^{222}\text{Rn}$ , causes  
4448 an increased fraction of radon to escape from its host mineral, a larger fraction than can be  
4449 explained by intramineral migration or diffusion.

4450 In groundwater, radium likely encounters dissolved sulfate and/or carbonate anions, which could  
4451 precipitate radium sulfate or radium carbonate. Although both salts are relatively insoluble, a  
4452 sulfate concentration of 0.0001 M would still allow an equilibrium concentration of about 0.1  
4453 ppm  $\text{Ra}^{+2}$  to exist in solution. Thus, the insolubilities of either of these salts are not likely to  
4454 prevent contamination of the environment.

4455 Radium also contaminates the environment because of past disposal practices of some proces-  
4456 sing, milling, and reclamation operations. Radium process tailings have been discovered in land  
4457 areas as seams or pockets of insoluble radium compounds, such as barium radium sulfate, or  
4458 unprocessed radium (uranium) ore, such as carnotite. Release of solid or liquid process streams  
4459 and subsequent mixing with local soil has resulted in intimate contamination of soil particles,  
4460 primarily as  $\text{Ra}^{+2}$  absorbed onto clay-sized fractions. This form of absorbed radium is tightly  
4461 bound to soil but can be extracted partially by hot concentrated acid solutions.

#### 4462 Solubility of Compounds

4463 The solubility of radium compounds can usually be inferred from the solubility of the correspon-  
4464 ding barium compound and the trend in the solubilities of the corresponding alkaline earth  
4465 compounds. The common water-soluble radium salts are the chloride, bromide, nitrate, and  
4466 hydroxide. The fluoride, carbonate, phosphate, biphosphate (hydrogen phosphate), and oxalate

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4467 are only slightly soluble. Radium sulfate is the least soluble radium compound known, insoluble  
4468 in water and dilute acids, but it is soluble in concentrated sulfuric acid, forming a complex ion  
4469 with sulfate anions,  $\text{Ra}(\text{SO}_4)_2^{-2}$ .

4470 Radium compounds are essentially insoluble in organic solvents. In most separation procedures  
4471 based on extraction, other elements, not radium, are extracted into the organic phase. Exceptions  
4472 are known (see "Separation," below), and crown ethers have been developed recently that  
4473 selectively remove radium from an aqueous environment.

### Review of Properties

4475 Radium is highly toxic exclusively because of its radioactive emissions: gamma radiation of the  
4476 element itself and beta particles emitted by some of its decay progeny. It concentrates in bones  
4477 replacing calcium and causing anemia and cancerous growths. Its immediate progeny, gaseous  
4478 radon, is an alpha emitter that is a health threat when inhaled.

4479 Metallic radium is brilliant white and reacts rapidly with air, forming a white oxide and black  
4480 nitride. It is an active metal that reacts with cold water to produce radium hydroxide, hydrogen,  
4481 and other products. The radium ion in solution is colorless. Its compounds also are colorless  
4482 when freshly prepared but darken and decompose on standing because of the intense alpha  
4483 radiation. The original color returns when the compound is recrystallized. Alpha emissions also  
4484 cause all radium compounds to emit a blue glow in air when sufficient quantities are available.  
4485 Radium compounds also are about 1.5 °C higher in temperature than their surroundings because  
4486 of the heat released when alpha particles lose energy on absorbance by the compound. Glass  
4487 containers turn purple or brown in contact with radium compounds and eventually the glass  
4488 crystallizes and becomes crazed.

4489 Like all alkaline earths, radium contains two valence electrons ( $7s^2$ ) and forms only +2 ions in its  
4490 compounds and in solution. The ionic radius of radium in crystalline materials is 152 pm (0.152  
4491 nm or 1.52 Å), the largest crystalline radius of the alkaline earth cations ( $\text{Ra}^{+2} > \text{Ba}^{+2} > \text{Sr}^{+2} >$   
4492  $\text{Ca}^{+2} > \text{Mg}^{+2} > \text{Be}^{+2}$ ). In contrast, the hydrated ion radius in solution is the smallest of the alkaline  
4493 earth cations, 398 pm ( $\text{Be}^{+2} > \text{Mg}^{+2} > \text{Ca}^{+2} > \text{Sr}^{+2} > \text{Ba}^{+2} > \text{Ra}^{+2}$ ). With the smallest charge-to-  
4494 crystal-radius ratio among the alkaline earths of 1.32 (+2/1.52), the smallest hydrated radius of  
4495 radium is expected, because the ratio represents the least attractive potential for water molecules  
4496 in solution.

4497 Solution Chemistry

4498 Existing exclusively in one oxidation state (+2), the chemistry of radium is uncomplicated by  
4499 oxidation-reduction reactions that could produce alternate states in solution. It is made even less  
4500 complicated by its weak tendency to form complex ions or hydrolyze in solution. These  
4501 properties are a reflection of the small charge-to-crystal-radius ratio of 1.32, described above. In  
4502 general, radiochemical equilibrium is established with carriers by stirring, followed by either  
4503 standing or digesting in the cold for several minutes. Adsorption of trace amounts of radium on  
4504 surfaces, however, is an important consideration in its radiochemistry.

4505 COMPLEXATION. Radium, like other alkaline-earth cations, forms few complexes in acid  
4506 solution. Under alkaline conditions, however, several one-to-one chelates are formed with  
4507 organic ligands: among others, with EDTA, diethylenetriaminepentaacetate (DTPA),  
4508 ethyleneglycol bis(2-aminoethylether)-tetraacetate (EGTA), nitrilotriacetate (NTA or NTTA),  
4509 and citrate. The most stable complex ion forms with DTPA. The tendency to form complexes  
4510 decreases as their crystalline size increases and their charge-crystal-radius ratio decreases. Since  
4511 crystalline sizes of the cations are in the order:  $Ra^{+2} > Ba^{+2} > Sr^{+2} > Ca^{+2}$ , radium has the least  
4512 tendency to form complex ions, and few significant complexes of radium with inorganic anions  
4513 are known. One notable exception is observed in concentrated sulfuric acid, which dissolves  
4514 highly insoluble radium sulfate ( $RaSO_4$ ) by forming  $Ra(SO_4)_2^{-2}$ .

4515 Complex-ion chemistry is not used in most radium radiochemical procedures. Complexing  
4516 agents are primarily employed as elution agents in cation exchange, in separations from barium  
4517 ions by fractional precipitation, and in titration procedures. Alkaline citrate solutions have been  
4518 used to prevent precipitation of radium in the presence of lead and barium carriers until complete  
4519 isotopic exchange has been accomplished.

4520 HYDROLYSIS. Similar to their behavior complex-ion formation, alkaline earths show less and less  
4521 tendency to hydrolyze with increasing size of the ions, and the tendency decreases with  
4522 increasing ionic strength of the solution. Therefore, hydrolysis of radium is an insignificant factor  
4523 in their solution chemistry.

4524 ADSORPTION. The adsorption of trace amounts of radium on surfaces is an important considera-  
4525 tion in its radiochemistry. Although not as significant with radium as with some ions with higher  
4526 charges, serious losses from solution can occur under certain conditions. Adsorption on glass is a  
4527 particular problem, and adsorption on polyethylene has been reported. Adsorption gradually  
4528 increases with increasing pH and depends strongly on the nature of the surface. In the extreme,  
4529 up to 50 percent radium has been observed to adsorb onto glass from neutral solution in 20 days,

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4530 and 30 percent from 0.13 M hydrochloric acid (HCl). Fortunately, adsorbed radium can be  
4531 removed from glass with strong acid.

4532 The presence of insoluble impurities, such as traces of dust or silica, increases adsorption, but  
4533 adsorption is negligible from very pure solutions at low pH values. Tracer radium solutions,  
4534 therefore, should be free from insoluble impurities, and radium should be completely in solution  
4535 before analysis. The solutions should also be maintained in at least 1 M mineral acid or contain  
4536 chelating agents. Addition of barium ion as a carrier for radium will probably decrease the  
4537 amount of radium adsorption. Radium residues from solubilization of samples that contain silica  
4538 or lead or barium sulfates and those that result in two or more separate solutions should be  
4539 avoided since the radium might divide unequally between the fractions. Destruction of silica with  
4540 HF, reduction of sulfates to sulfides with zinc dust, and subsequent dissolution of the residue  
4541 with nitric acid are procedures used to avoid this problem.

### 4542 Dissolution of Samples

4543 Soil, mineral, ore samples, and other inorganic solids are dissolved by conventional treatment  
4544 with mineral acids and by fusion with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Hydrofluoric acid (HF) or  
4545 potassium fluoride (KF) is used to remove silica. Up to 95 percent radium removal has been  
4546 leached from some samples with hot nitric acid ( $\text{HNO}_3$ ), but such simple treatment will not  
4547 completely dissolve all the radium in soil, rock, and mineral samples. Biological samples are wet  
4548 ashed first with mineral acids or decomposed by heating to remove organic material. The residue  
4549 is taken up in mineral acids or treated to remove silica. Any dissolution method that results in  
4550 two or more separate fractions should be avoided, since the adsorption characteristics of trace  
4551 quantities of radium may cause it to divide between the fractions.

4552 Barium sulfate ( $\text{BaSO}_4$ ), often used to coprecipitate radium from solution, can be dissolved  
4553 directly into alkaline EDTA solutions. Radium can be repeatedly reprecipitated and dissolved by  
4554 alternate acidification with acetic acid and dissolution with the EDTA solution.

4555 Solutions resulting from dissolution of solid samples should be made at least 1 M with mineral  
4556 acid before storage to prevent radium from absorbing onto the surface of glass containers.

### 4557 Separation Methods

4558 COPRECIPITATION. Radium is almost always present in solution in trace amounts, and even the  
4559 most insoluble radium compound, radium sulfate, can not be used to separate and isolate radium  
4560 from solution by direct precipitation. Therefore, the cation is commonly removed from solution

4561 in virtually quantitative amounts by coprecipitation. Since radium forms the same types of  
4562 insoluble compounds as barium: sulfates ( $\text{SO}_4^{-2}$ ), chromates ( $\text{CrO}_4^{-2}$ ), carbonates ( $\text{CO}_3^{-2}$ ),  
4563 phosphates ( $\text{PO}_4^{-3}$ ), oxalates ( $\text{C}_2\text{O}_4^{-2}$ ), and sulfites ( $\text{SO}_3^{-2}$ ), it coprecipitates with all insoluble  
4564 barium compounds, and to a lesser extent with most insoluble strontium and lead compounds.  
4565 Barium sulfate and barium chromate are most frequently used to carry radium during coprecipita-  
4566 tion. Other compounds that are good carriers for radium include: ferric hydroxide when  
4567 precipitated at moderately high pH with sodium hydroxide (NaOH) or ammonium hydroxide  
4568 ( $\text{NH}_4\text{OH}$ ), barium chloride ( $\text{BaCl}_2$ ) when precipitated from a cold mixed solvent of water and  
4569 alcohol saturated with hydrochloric acid, barium iodate ( $\text{BaIO}_3$ ), and various insoluble  
4570 phosphates, fluorides ( $\text{F}^{-1}$ ), and oxalates (e.g., thorium phosphate [ $\text{Th}_3(\text{PO}_4)$ ], lanthanum fluoride  
4571 ( $\text{LaF}_3$ ), and thorium oxalate [ $\text{Th}(\text{C}_2\text{O}_4)$ ]). Lead sulfate ( $\text{PbSO}_4$ ) can be used if a carrier-free radium  
4572 preparation is required, since quantitative lead-radium separations are possible while quantitative  
4573 barium-radium separations are very difficult.

4574 ION EXCHANGE. Radium has been separated from other metals on both cation- and anion-  
4575 exchange resins. Barium and other alkaline earths are separated on cation-exchange columns  
4576 under acidic conditions. In dilute hydrochloric acid solutions (3 M), the affinity of the cation for  
4577 the exchange site is dominated by ion-dipole interactions between the water molecules of the  
4578 hydrated ion and the resin. Ions of smaller hydrated radius (smaller charge-to-crystal-radius ratio)  
4579 tend to displace ions of larger hydrated radius. The affinity series is  $\text{Ra}^{+2} > \text{Ba}^{+2} > \text{Sr}^{+2} > \text{Ca}^{+2}$ , and  
4580 radium elutes last. Increasing the acid concentration to 12 M effectively reverses the order of  
4581 affinity, since the strong acid tends to dehydrate the ion, and ion-resin affinity is dominated more  
4582 by ionic interactions, increasing in the order of increasing crystal radius:  $\text{Ca}^{+2} > \text{Sr}^{+2} > \text{Ba}^{+2} > \text{Ra}^{+2}$ ,  
4583 and calcium elutes last. Radium has also been separated from tri- and tetravalent ions since these  
4584 ions have a much stronger affinity for the cation-exchange resin. Radium with its +2 charge is  
4585 only partially absorbed, while trivalent actinium and tetravalent thorium, for example, will be  
4586 completely absorbed. Tracer quantities of radium also has been separated from alkaline earths by  
4587 eluting a cation-exchange column with chelating agents such as lactate, citrate, and EDTA;  
4588 radium typically elutes last, since it forms weaker interactions with the ligands.

4589 Anion-exchange resins have been used to separate radium from other metal ions in solutions of  
4590 chelating agents that form anionic complexes with the cations. The affinity for the columns  
4591 decreases in the order  $\text{Ca} > \text{Sr} > \text{Ba} > \text{Ra}$ , reflecting the ability of the metal ions to form stable  
4592 complex anions with the chelating agents. The difficult separation of barium from radium has  
4593 been accomplished by this procedure. Radium is also separated from metals such as uranium,  
4594 polonium, bismuth, lead, and protactinium that form polychloro complex anions. Since radium  
4595 does not form a chlorocomplex, it does not absorb on the anion exchanger (carrying a positive  
4596 charge), and remains quantitatively in the effluent solution.

4597 Ion-exchange methods are not easily adapted for the separation of macro-scale quantities of  
4598 radium, because the intense radiation degrades the synthetic resin and insoluble radium  
4599 compounds usually form in the ion-exchange column.

4600 SOLVENT EXTRACTION. Radium compounds have very low solubilities in organic solvents. In  
4601 most extraction procedures, other organic-soluble complexes of elements, not radium, are  
4602 extracted into the non-aqueous phase, leaving radium in the water. Radium is separated from  
4603 actinium, thorium, polonium, lead, bismuth, and thallium, for example, by extracting these  
4604 elements as 2-thenoyltrifluoroacetone (TTA) complexes. Radium does not form the complex  
4605 except at very high pH, and is not extracted. One notable exception to this generality is the  
4606 extraction of radium tetraphenylborate by nitrobenzene from an alkaline solution. The presence  
4607 of EDTA inhibits formation of the tetraphenylborate, however, and radium is not extracted in the  
4608 presence of EDTA either.

4609 More recent developments have employed crown ethers to selectively extract radium as a  
4610 complex ion from water samples for analysis. Radium-selective extraction membranes have also  
4611 been used to isolate radium from solutions.

#### 4612 Methods of Analysis

4613 Radium is detected and quantified by counting either alpha or gamma emissions of the  
4614 radionuclide or its progeny. Gamma-ray spectroscopy can be used on macro  $^{226}\text{Ra}$  samples  
4615 (approximately 50 g or more) without pretreatment unless  $^{235}\text{U}$ , even in very small quantities, is  
4616 present to interfere with the measured peak. The most sensitive method for the analysis of  $^{226}\text{Ra}$   
4617 is de-emanation of  $^{222}\text{Rn}$  from the radium source, complete removal, followed by alpha counting  
4618 the  $^{222}\text{Rn}$  and its progeny. The procedure is lengthy and expensive, however. The radium in a  
4619 liquid sample is placed in a sealed tube for a specified time to allow the ingrowth of  $^{222}\text{Rn}$ . The  
4620 radon is collected in a scintillation cell and stored for several hours to allow for ingrowth of  
4621 successive progeny products. The alpha radiation is then counted in the scintillation cell called a  
4622 Lucas cell. The primary alpha emissions are from  $^{222}\text{Rn}$ ,  $^{218}\text{Po}$ , and  $^{214}\text{Po}$ . Complete retention of  
4623 radon can also be accomplished by sealing the radium sample hermetically in a container and  
4624 alpha- or gamma-counting.

4625  $^{228}\text{Ra}$  can also be determined directly by gamma spectroscopy, using the gamma-rays of its  
4626 progeny,  $^{228}\text{Ac}$ , without concern for interference; however, a lower detection limit is obtained if  
4627 the  $^{228}\text{Ac}$  is measured by beta counting. In the beta-counting procedure,  $^{228}\text{Ra}$  is separated, time is  
4628 allowed for actinium ingrowth, the  $^{228}\text{Ac}$  is removed by solvent extraction, ion-exchange, or  
4629 coprecipitation, and then measured by beta counting.

4630  $^{224}\text{Ra}$  can be determined by chemically isolating the  $^{212}\text{Pb}$ , which is in equilibrium with the  $^{224}\text{Ra}$ .  
4631 After an appropriate ingrowth period,  $^{212}\text{Pb}$  is determined by alpha counting its progeny,  $^{212}\text{Bi}$  and  
4632  $^{212}\text{Po}$ .

4633 Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Considine and Considine,  
4634 1983; DOE, 1990 and 1997, 1997; EPA, 1984; Friedlander et al., 1981; Green and Earnshaw,  
4635 1984; Hassinsky and Asloff, 1965; Kirby and Salutsky, 1964; Lindsay, 1988; Salutsky, 1997;  
4636 Sedlet, 1966; Shoesmith, 1964; Sunderman and Townley, 1960; Turekian and Bolter, 1966;  
4637 Vdovenko and Dubasov, 1975.

#### 4638 14.10.9.7 Strontium

4639 Strontium, atomic number 38, is the fourth member of the alkaline-earth metals, which includes  
4640 beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).  
4641 Like radium, it exist exclusively in the +2 oxidation state in both compounds and in solution,  
4642 making its chemistry simpler than many of the radionuclides reviewed in this section.

#### 4643 Isotopes

4644 Strontium exists in 29 isotopic forms, including three metastable states, ranging in mass number  
4645 from 77 to 102. Natural strontium is a mixture of four stable isotopes:  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$ , and  $^{88}\text{Sr}$ .  
4646 The lower mass number isotopes decay by electron capture, and the isotopes with higher mass  
4647 numbers are primarily beta emitters. The half-lives of most isotopes are short, measured in  
4648 milliseconds, seconds, minutes, hours, or days. The exception is  $^{90}\text{Sr}$ , a beta emitter with a half-  
4649 life of 29.1 years.

#### 4650 Occurrence and Uses

4651 Strontium is found in nature in two main ores, celestite ( $\text{SrSO}_4$ ) and strontianite ( $\text{SrCO}_3$ ), widely  
4652 distributed in small concentrations. Small amounts are found associated with calcium and barium  
4653 minerals. The earth's crust contains 0.042 percent strontium, ranking twenty-first among the  
4654 elements occurring in rock and making it as abundant as chlorine and sulfur. The element ranks  
4655 11<sup>th</sup> in abundance in sea water, about 8-10 ppm. The only naturally occurring radioactive isotopes  
4656 of strontium are the result of spontaneous fission of uranium in rocks. Other nuclear reactions  
4657 and fallout from nuclear weapons test are additional sources of fission products.  $^{90}\text{Sr}$  is a fission  
4658 product of  $^{235}\text{U}$ , along with  $^{89}\text{Sr}$ , and short-lived isotopes,  $^{91}\text{Sr}$  to  $^{102}\text{Sr}$ .  $^{85}\text{Sr}$  can be produced by  
4659 irradiation of  $^{85}\text{Rb}$  with accelerated protons or deuterons.

## Separation Techniques

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4660 Stable strontium is produced from its ores. The sulfate ore is leached with hydrochloric acid  
4661 solution to remove impurities and shaken with sodium carbonate for several hours to produce  
4662 strontium carbonate. Washing this product or the carbonate ore with hot water and several  
4663 reprecipitation steps produce a fine grade of strontium carbonate. The metal is produced by  
4664 converting the carbonate to strontium chloride with hydrochloric acid or to strontium oxide by  
4665 heating. Strontium chloride in a melt with potassium chloride is electrolyzed or the oxide is  
4666 reduced by heating with aluminum in a vacuum to distill off the metal. An alternate method  
4667 electrolyzes an aqueous solution of the chloride with a mercury cathode. The resultant mercury  
4668 amalgam is heated in hydrogen to drive off the mercury.

4669 The major use of strontium is in glass production for color television picture tubes. Strontium is  
4670 used in producing ferrite magnets, in refining zinc, to produce hardness and durability in alloys of  
4671 tin and lead, as a deoxidizer in copper and bronze, and “getter” in electron tubes. Strontium  
4672 hydroxide forms soaps and greases with numerous organic acids that are stable, resistant to  
4673 oxidation and decomposition over a wide temperature range, and resistant to decomposition by  
4674 water and the leaching action of hydrocarbons. The beta emission of  $^{90}\text{Sr}$  and its progeny,  $^{90}\text{Y}$   
4675 ( $t_{1/2}=64$  h), has found applications in industry, medicine, and research. The radionuclides are in  
4676 equilibrium in about 25 days. The radiation of  $^{90}\text{Y}$  is more penetrating than that of strontium. It is  
4677 used with zinc sulfide in some luminescent paints. Implants of  $^{90}\text{Sr}$  provide radiation therapy for  
4678 the treatment of the pituitary gland and breast and nerve tissue. The radiation from strontium has  
4679 been used in thickness gauges, level measurements, automatic control processes, diffusion  
4680 studies of seawater, and a source of electrical power. Since  $^{90}\text{Sr}$  is one of the long-lived and most  
4681 energetic beta emitters, it might prove to be a good source of power in space vehicles, remote  
4682 weather stations, navigational buoys, and similar long-life, remote devices. Both  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$   
4683 have been used in physical chemistry experiments and in biology as tags and tracers.  $^{90}\text{Sr}$  to  $^{87}\text{Sr}$   
4684 ratios are used in geological dating, because  $^{87}\text{Sr}$  is formed by decay of long-lived  $^{87}\text{Rb}$ .

### Solubility of Compounds

4686 Several simple salts of strontium are soluble in water. Among these are the acetate, chloride,  
4687 bromide, iodide, nitrate, nitrite, permanganate, sulfide, chlorate, bromate, and perchlorate.  
4688 Strontium hydroxide is slightly soluble and is precipitated only from concentrated solutions.

### Review of Properties

4690 Strontium is a low-density ( $2.54 \text{ g/cm}^3$ ) silver-white metal. It is as soft as lead and is malleable  
4691 and ductile. Three allotropic forms exist with transition temperatures of 235 and 540 °C. Freshly

4692 cut strontium is silver in appearance, but it rapidly turns a yellowish color on formation of the  
4693 oxide in the air. It is stored under mineral oil to prevent oxidation.

4694 The metal decomposes water, producing strontium hydroxide [Sr(OH)<sub>2</sub>] and hydrogen, and the  
4695 finely divided metal ignites spontaneously in the air. The hydroxide forms strontium peroxide  
4696 (SrO<sub>2</sub>) when treated with hydrogen peroxide in the cold. Strontium is a strong reducing agent and  
4697 combines directly with hydrogen, halogens, oxygen, and sulfur to form, respectively, the simple  
4698 binary compounds: hydride (SrH<sub>2</sub>), halogens (SrX<sub>2</sub>), oxide (SrO), and sulfide (SrS). The metal  
4699 reacts with nitrogen to form the nitride (Sr<sub>3</sub>N<sub>2</sub>) only on heating to 380 °C. It also reacts  
4700 vigorously with most acids to form Sr<sup>+2</sup> salts and hydrogen. With nitric acid the reaction is fast,  
4701 producing nitrogen dioxide. In contrast, reaction with sulfuric acid is slow because of the  
4702 formation of the insoluble sulfate [Sr(SO<sub>4</sub>)<sub>2</sub>].

4703 Strontium isotopes are some of the principal constituents of radioactive fallout following  
4704 detonation of nuclear weapons, and they are released in insignificant amounts during normal  
4705 operations of reactors and fuel reprocessing operations. Their toxicity is higher, however, than  
4706 that of other fission products, and <sup>90</sup>Sr represent a particular hazard because of its long half-life,  
4707 energetic beta emission, tendency to contaminate food, especially milk, and high retention in  
4708 bone structure. Strontium in bone is difficult to eliminate and has a biological half-life of  
4709 approximately eleven years (4,000 d).

4710 Strontium occurring in groundwater is primarily in the form of strontium carbonate. Its solubility  
4711 under oxidizing and reducing conditions is approximately 0.001 M (0.15 g/L or 150 g/m<sup>3</sup>).

#### 4712 Solution Chemistry

4713 Strontium exists exclusively in the +2 oxidation state in solution, so the chemistry of strontium is  
4714 uncomplicated by oxidation-reduction reactions that could produce alternate states in solution.

4715 COMPLEXATION. Strontium has little tendency to form complexes. Of the few complexing agents  
4716 for strontium, the significant agents in radiochemistry to date are EDTA, oxalate, citrate,  
4717 ammoniacetate, methylanine-N,N-diacetate, 8-quinolinol, and an insoluble chelate with  
4718 picrolonate. The most stable complex ion forms with EDTA. Coordination compounds of  
4719 strontium are not common. These chelating agents are used primarily in ion-exchange  
4720 procedures. Amine chelates of strontium are unstable, and the β-diketones and alcohol chelates  
4721 are poorly characterized. In contrast, cyclic crown ethers and cryptates form stronger chelates  
4722 with strontium than with calcium, the stronger chelating metal with EDTA and more traditional  
4723 chelating agents. Cryptates are a macrocyclic chelate of the type, N[(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>N, an

## Separation Techniques

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4724 octadentate ligand containing six oxygen atoms and two nitrogen atoms as ligand bonding sites  
4725 that encapsulates the cation. It might find use in the extraction chemistry of strontium.

4726 HYDROLYSIS. The tendency of the alkaline-earth cations to hydrolyze decreases as their atomic  
4727 number increases. The tendency is greater than that of the corresponding alkali metals, but  
4728 hydrolysis of potassium, for example, is insignificant. An indication of the tendency of a cation  
4729 to hydrolyze is the solubility of their hydroxides, and the solubility of the alkaline earths become  
4730 more soluble with increasing atomic number. Strontium hydroxide is slightly soluble in water (8  
4731 g/L at 20 °C). In comparison, the hydroxide of beryllium, the first element in the alkaline earth  
4732 series, has a solubility of approximately  $3 \times 10^{-4}$  g/L.

### 4733 Dissolution of Samples

4734 Dissolution of samples for the analysis of strontium is generally simple. Water is used to dissolve  
4735 soluble compounds: acetate, bromide, chloride, iodide, chlorate, perchlorate, nitrate, nitrite, and  
4736 permanganate. Hydrochloric or nitric acid dissolves the fluoride, carbonate, oxalate, chromate,  
4737 phosphate, sulfate, and oxide. Strontium in limestone, cement, soil, bone, and other biological  
4738 material can be dissolved from some samples in hot hydrochloric acid. Insoluble silica, if present,  
4739 can be filtered or centrifuged. In some cases, soil can be leached to remove strontium. As much  
4740 as 99.5 percent of the strontium in some crushed soil samples has been leached with 1 M nitric  
4741 acid by three extractions. Soil samples have also been suspended overnight in ammonium acetate  
4742 at pH 7. If leaching is not successful, soil samples can be dissolved by alkali fusion of the ground  
4743 powder with potassium hydroxide, nitrate, or carbonate. Strontium is taken up from the residue  
4744 in nitric acid. Biological materials such as plant material or dairy products are solubilized by  
4745 ashing at 600 °C and taking up milk residue in hot, concentrated hydrochloric acid and plant  
4746 residue in aqua regia. Wet ashing can be used by treating the sample with nitric acid followed by  
4747 an equal-volume mixture of nitric and perchloric acids. Human and animal bone samples are  
4748 ashed at 900 °C and the residue dissolved in concentrated hydrochloric acid.

### 4749 Separation Methods

4750 PRECIPITATION AND COPRECIPITATION. The common insoluble salts of strontium are the fluoride,  
4751 carbonate, oxalate, chromate, and sulfate. Most are suitable for radiochemical procedures, and  
4752 strontium separation have the advantage of stable forms of strontium that can be used as a carrier  
4753 and are readily available. Precipitation of strontium nitrate in 80 percent nitric acid has been used  
4754 to separate stable strontium carrier and  $^{90}\text{Sr}$  from its progeny,  $^{90}\text{Y}$ , and other soluble nitrates  
4755 (calcium, for example). The solubility of strontium chloride in concentrated hydrochloric  
4756 solution has been used to separate strontium from barium—barium chloride is insoluble in the

4757 acid. Barium and radium (as coprecipitant) have been removed from strontium by precipitating  
4758 barium as the chromate at a carefully controlled pH of 5.5. Strontium chromate will not  
4759 precipitate unless the pH is raised. Strontium can also be separated from yttrium by precipitation  
4760 of the much less soluble yttrium hydroxide by raising an acid solution of the cations to a pH of  
4761 about 8 with ammonium hydroxide. Strontium hydroxide is slightly soluble and will not  
4762 precipitate without high concentrations of hydroxide or strontium or both. Carrier-free strontium  
4763 is coprecipitated with ferric hydroxide, and lead sulfate is also used.

4764 SOLVENT EXTRACTION. The application of organic solvents for separation of strontium from  
4765 other metals has not been extensive. Thenoyltrifluoroacetone (TTA) has been used to extract  
4766 carrier-free strontium at a pH > 10. At pH 5, <sup>90</sup>Y is extracted with TTA from strontium, which  
4767 remains in aqueous solution. 8-hydroxyquinolinol in chloroform has also been used to extract  
4768 strontium. The few procedures that have been available are mainly used to separate the alkaline  
4769 earths from each other. A 1:1 mixture of ethyl alcohol and diethyl ether extracts calcium from  
4770 strontium.

4771 In recent years, extraction procedures have been developed based on the complexation of  
4772 strontium cations with crown ethers in 1-octanol. Strontium can be extracted with these mixture  
4773 from 1 M to 7 M nitric acid solutions. The most advantageous application of strontium extraction  
4774 procedures has been found in extraction chromatography. An extraction resin consisting of  
4775 4,4'(5')-bis(*t*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) in 1-octanol on an inert polymeric  
4776 matrix is highly selective for strontium nitrate and will separate the cation from many other  
4777 metals including calcium, barium, and yttrium. This column is used to separate strontium from  
4778 potassium, cerium, plutonium, and neptunium (K<sup>+</sup>, Ce<sup>4+</sup>, Pu<sup>4+</sup>, Np<sup>4+</sup>, respectively). The column  
4779 is prepared and loaded from 8 M nitric acid. The ions listed above are eluted with 3 M nitric acid  
4780 containing oxalic acid. Strontium is eluted with 0.05 M nitric acid.

4781 ION-EXCHANGE CHROMATOGRAPHY. Ion-exchange chromatography is used to separate trace  
4782 quantities of strontium, but separation of macro quantities is very time consuming. Strontium is  
4783 absorbed on cation-exchange resins, and elution is often based on the formation of a stable  
4784 complex. Carrier-free strontium is separated from fission products, including barium, on a  
4785 cation-exchange resin and eluted with citrate. In a similar process, strontium was also separated  
4786 from other alkaline earths, magnesium, calcium, barium, and radium, eluting with ammonium  
4787 lactate at pH 7 and 78 °C. Good separations were also obtained with hydrochloric solutions and  
4788 ammonium citrate. <sup>90</sup>Sr and <sup>90</sup>Y are separated on a cation-exchange column, eluting yttrium with  
4789 ammonium citrate at pH 3.8 and strontium at pH 6.0. Strontium and calcium have also been  
4790 separated in EDTA solutions at pH 5.3. Strontium is retained on the column, and calcium elutes  
4791 as the calcium-EDTA complex. Strontium elutes with 3 M hydrochloric acid.

## Separation Techniques

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4792 Not many procedures use anion-exchange chromatography for separation of strontium.  $^{90}\text{Sr}$  has  
4793 been separated from  $^{90}\text{Y}$  on an anion-exchange resin pretreated with hydroxide. Strontium is  
4794 eluted from the column with water, and yttrium is eluted with 1 M hydrochloric acid. The  
4795 alkaline earths have been separated by anion-exchange column pretreated with dilute ammonium  
4796 citrate, loading the column with the chloride form of the metals, and eluting with ammonium  
4797 citrate at pH 7.5.

### 4798 Methods of Analysis

4799 Macroquantities of strontium are determined by gravimetric methods and atomic absorption  
4800 spectrometry, and emission spectrometry. Strontium is precipitated as strontium carbonate or  
4801 sulfate in gravimetric procedures. For atomic absorption analysis, the separated sample is ashed,  
4802 and the product is dissolved in hydrochloric acid. Lanthanum is added to the solution to  
4803 precipitate interfering anions, phosphate, sulfate, or aluminate, that would occur in the flame.

4804  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  are determined by analysis of their beta emissions. With a short half-life of 53 d,  
4805  $^{89}\text{Sr}$  is only found in fresh fission products.  $^{90}\text{Sr}$  is a beta emitter with a half-life of 27.7 y. Its  
4806 progeny is  $^{90}\text{Y}$ , which emits beta particles with a half-life of 64.0 h, producing stable  $^{90}\text{Zr}$ .  
4807 Neither  $^{90}\text{Sr}$  nor  $^{90}\text{Y}$  is a gamma emitter.  $^{90}\text{Sr}$  is determined directly from its beta emission, before  
4808  $^{90}\text{Y}$  grows in, by beta counting immediately (three to four hours) after it is collected by  
4809 precipitation. The chemical yield can be determined gravimetrically by the addition of stable  
4810 strontium, after the separation of calcium. Alternatively,  $^{90}\text{Sr}$  can be measured from the beta  
4811 emission of  $^{90}\text{Y}$  while it reaches secular equilibrium (two to three weeks). The  $^{90}\text{Y}$  is separated by  
4812 solvent extraction and evaporated to dryness or by precipitation, then beta counted. The chemical  
4813 yield of the yttrium procedure can be determined by adding stable yttrium and determining the  
4814 yttrium gravimetrically.  $^{89}\text{Sr}$  has a half-life of 52.7 d and is only present in fresh fission material.  
4815 If it is present with  $^{90}\text{Sr}$ , it can be determined by the difference in activity of combined  $^{89}\text{Sr}$  and  
4816  $^{90}\text{Sr}$  (combined or total strontium) and the activity of  $^{90}\text{Sr}$ . Total strontium is measured by beta  
4817 counting immediately after it is collected by precipitation, and  $^{90}\text{Sr}$  is measured by isolating  $^{90}\text{Y}$   
4818 after ingrowth.  $^{85}\text{Sr}$  can be used as a tracer for determining the chemical yield of  $^{90}\text{Sr}$  (determined  
4819 by isolating  $^{90}\text{Y}$ ), but its beta emission interferes with beta counting of total strontium and must  
4820 be accounted for in the final activity.

4821 An alternative method for determining  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  in the presence of each other is based on the  
4822 equations for decay of strontium radionuclides and ingrowth of  $^{90}\text{Y}$ . Combined strontium is  
4823 collected and immediately counted to determine the total strontium. During ingrowth, the  
4824 mixture is recounted, and the data from the counts are used to determine the amount of  $^{89}\text{Sr}$  and  
4825  $^{90}\text{Sr}$  in the original (fresh) mixture.

4826 Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Considine and Considine,  
4827 1983; CRC, 1998-99; DOE, 1990 and 1997, 1997; EPA, 1973; EPA, 1980; Greenwood and  
4828 Earnshaw, 1984; Hassinsky and Adloff, 1965; Riley, 1995; Sunderman and Townley, 1960;  
4829 Turekian and Bolter, 1966.

#### 4830 14.10.9.8 Technetium

4831 Technetium, atomic number 43, was the first element to be made artificially. Technetium has no  
4832 stable isotopes. Natural technetium is known to exist but only in negligibly small quantities  
4833 resulting from the spontaneous fission of natural uranium. Technetium is chemically very similar  
4834 to rhenium, but significant differences exist that cause them to behave quite differently under  
4835 certain conditions.

#### 4836 Isotopes

4837 Thirty-one radioisotopes and unstable isomers of technetium are known with mass numbers  
4838 ranging from 86 to 113. The half-lives range from seconds to millions of years. The lower mass  
4839 number isotopes decay by primarily by electron capture and the higher mass number isotopes by  
4840 beta emission. The significant isotopes (with half-lives/decay modes) are  $^{95m}\text{Tc}$  (61 d/electron  
4841 capture and isomeric transition),  $^{99m}\text{Tc}$  (6.01 h/isomeric transition by low-energy gamma), and  
4842  $^{99}\text{Tc}$  ( $2.13 \times 10^5$  y/beta to stable ruthenium-99). Other, long-lived isotopes are  $^{97}\text{Tc}$  ( $2.6 \times$   
4843  $10^6$ /electron-capture) and  $^{98}\text{Tc}$  ( $4.2 \times 10^6$  y/beta emission).

#### 4844 Occurrence and Uses

4845 The first synthesis of technetium was through the production of  $^{99}\text{Mo}$  by bombardment of  $^{98}\text{Mo}$   
4846 with neutrons and subsequent beta decay to  $^{99}\text{Tc}$ . Technetium is also a major constituent of  
4847 nuclear reactor fission products and has been found in very small quantities in pitchblende from  
4848 the spontaneous fission of naturally occurring uranium.

4849 Technetium makes up about 6 percent of uranium fission products in nuclear power plant fuels. It  
4850 is recovered from these fuels by solvent extraction and ion-exchange after storage of the fuels for  
4851 several years to allow the highly radioactive, short-lived products to decay. Technetium is  
4852 recovered as ammonium pertechnetate ( $\text{NH}_4\text{TcO}_4$ ) after its solutions are acidified with  
4853 hydrochloric acid, precipitated with sulfide, and the sulfide ( $\text{Tc}_2\text{S}_7$ ) is reacted with hydrogen  
4854 peroxide. Rhenium and molybdenum are also removed by extraction with organic solvents. The  
4855 metal is obtained by reduction of ammonium pertechnetate with hydrogen at 600 °C.

## Separation Techniques

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4856 Potassium pertechnates ( $\text{KTcO}_4$ ) have been used in water (55 ppm) as corrosion inhibitors for  
4857 mild carbon steel in aerated distilled water, but currently there is no significant uses of elemental  
4858 technetium or its compounds, although technetium and some of its alloys are a superconductor.  
4859 The corrosion protection is limited to closed systems to prevent release of the radioactive isotope.  
4860  $^{99\text{m}}\text{Tc}$ , with a half-life of only 61 days, has been used in tracer work.  $^{99\text{m}}\text{Tc}$  is used in medical  
4861 diagnosis as a radioactive tracer. As a complex, the amount of  $^{99\text{m}}\text{Tc}$  required for gamma  
4862 scanning is very small, thus, it is referred to as non-invasive scanning. It is used for cardiovascu-  
4863 lar and brain studies and the diagnosis of liver, spleen, and thyroid disorders. There are more than  
4864 20  $^{99\text{m}}\text{Tc}$  compounds available commercially for diagnostic purposes. With iodine isotopes, they  
4865 are the most frequently used radionuclides for diagnostics.  $^{99\text{m}}\text{Tc}$  has also been used to determine  
4866 the deadtime of counting detectors.

### 4867 Solubility of Compounds

4868 The nature of the compounds has not been thoroughly delineated, but ammonium pertechnetate  
4869 is soluble in water, and technetium heptoxide forms soluble pertechnetic acid ( $\text{HTcO}_4$ ) when  
4870 water is added.

### 4871 Review of Properties

4872 Technetium is a silver-grey metal that resembles platinum in appearance. It tarnishes slowly in  
4873 moist air to give the oxyacid, pertechnetic acid ( $\text{HTcO}_4$ ). It has a density of  $11.5 \text{ g/cm}^3$ . The metal  
4874 reacts with oxygen at elevated temperatures to produce the volatile oxide, technetium heptoxide.  
4875 Technetium dissolves in warm bromine water, nitric acid, aqua regia, and concentrated sulfuric  
4876 acid, but it is insoluble in hydrochloric and hydrofluoric acids. Technetium forms the chlorides  
4877 ( $\text{TcCl}_4$  and  $\text{TcCl}_6$ ) and fluorides ( $\text{TcF}_5$  and  $\text{TcF}_6$ ) by direct combination of the metal with the  
4878 respective halogen. The specific halide is obtained by selecting the proper temperature and  
4879 pressure for its formation.

4880  $^{99}\text{Tc}$  has a high specific activity. As a contamination hazard, it should be handled in a glove box.

4881 The behavior of technetium in groundwater is highly dependent on its oxidation state. Under  
4882 oxidizing conditions, pertechnate is the predominant species. It is very soluble and only slightly  
4883 absorbed to mineral components. For those reasons, it has a relatively high dissemination  
4884 potential in natural systems. Under reducing conditions, technetium precipitates as technetium  
4885 dioxide ( $\text{TcO}_2$ ), which is very insoluble. With the production of  $^{99}\text{Tc}$  in fission fuels and  
4886 considering its long half-life, the soluble form of the radionuclide is an environmental concern  
4887 wherever the fuel is reprocessed or stored. As a consequence,  $^{99}\text{Tc}$  would be expected to be one

4888 of the principle contributors to a radioactive release to the environment, even from repositories  
4889 with barriers that could retain the radionuclide up to 10,000 years. Studies of a salt repository  
4890 indicate that  $^{99}\text{Tc}$  is one of the few radionuclides that might reach the surface before it decays.

4891 Solution Chemistry

4892 All oxidation states between -1 and +7 can be expected for technetium, but the important ones in  
4893 solution are +4 and +7. The +4 state exist primarily as the slightly soluble oxide,  $\text{TcO}_2$ . It is  
4894 soluble only in the presence of complexing ligands;  $\text{TcCl}_6^{-2}$ , for example, is stable in solutions  
4895 with a chloride concentration greater than 1 M. The most important species in solution is the  
4896 pertechnetate ion [ $\text{TcO}_4^{-1}$  as  $\text{Tc(VII)}$ ], which is readily soluble and easily formed from lower  
4897 oxidation states with oxidizing agents such as nitric acid and hydrogen peroxide. There is no  
4898 evidence of polymeric forms in solution as a result of hydrolysis of the metal ion.

4899 OXIDATION-REDUCTION BEHAVIOR. Most radioanalytical procedures for technetium are  
4900 performed on the pertechnetate ion,  $\text{TcO}_4^{-1}$ . The ion can be reduced by hydrochloric acid, the  
4901 thiocyanate ion ( $\text{SCN}^{-1}$ ), organic impurities, anion-exchange resins, and some organic solvents.  
4902 The product of reduction can be  $\text{TcO}_2$  [ $\text{Tc(IV)}$ ], although a multiplicity of other products are  
4903 expected in complexing media. Even though the +7 oxidation state is easy to reduce, the  
4904 reduction process is sometimes slow. Unless precautions are taken to maintain the appropriate  
4905 oxidation state, however, erratic results will be obtained during the radioanalytical procedure.  
4906 Several examples illustrate the precaution. Dissolution should always be performed under  
4907 strongly oxidizing conditions to ensure conversion of all states to the +7 oxidation state since  
4908 complications because of slow exchange with carrier and other reagents are less likely to occur if  
4909 this state is maintained. Technetium is extracted with various solvents in several radioanalytical  
4910 procedures, but the method can be very inefficient because of reduction of the pertechnetate ion by  
4911 some organic solvents. The presence of an oxidizing agent such as hydrogen peroxide will  
4912 prevent the unwanted reduction. In contrast,  $\text{TcO}_4^{-1}$  is easily lost on evaporation of acid solutions  
4913 unless a reducing agent is present or evaporation is conducted at a relatively low temperature.

4914 COMPLEXATION. Technetium forms complex ions in solution with several simple inorganic  
4915 ligands such as fluoride and chloride. The +4 oxidation state is represented by the  $\text{TcX}_6^{-2}$  ion  
4916 where X = F, Cl, Br, and I. It is formed from  $\text{TcO}_4^{-1}$  by reduction to the +4 state with iodide in  
4917 HX.  $\text{TcF}_6^{-2}$  is found in HF solutions during decomposition of samples, before further oxidation.

4918 Complex ions formed between organic ligands and technetium in the +5 oxidation state are  
4919 known with the general formula,  $\text{TcO}_3\text{XLL}$ , where X is a halide and L is an organic ligand. the

## Separation Techniques

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4920 ligands typically bond through an oxygen or nitrogen atom. Other organic complexes of the +5  
4921 state have the general formulas:  $\text{TcOX}_2\text{L}_2$ ,  $\text{TcOX}_4^{-1}$ , and  $\text{TcOX}_5^{-2}$ .

### 4922 Dissolution of Samples

4923 Dissolution of samples containing technetium requires two precautions: it is essential that acid  
4924 solutions be heated only under reflux conditions to avoid losses by volatilization, and dissolution  
4925 should be done only with strongly oxidizing conditions to ensure conversion of all lower  
4926 oxidation states to Tc(VII). In addition, problems with slow carrier exchange are less likely for  
4927 the VII oxidation state. Molybdenum targets are dissolved in nitric acid or aqua regia, but the  
4928 excess acid interferes with many subsequent analytical steps. Dissolution in concentrated sulfuric  
4929 acid followed by oxidation with hydrogen peroxide after neutralization avoids these problems of  
4930 excess acid. Other technetium samples can be dissolved by fusion with sodium peroxide/sodium  
4931 hydroxide ( $\text{Na}_2\text{O}_2/\text{NaOH}$ ) fluxes.

### 4932 Separation Methods

4933 PRECIPITATION AND COPRECIPITATION. The various oxidation states of technetium are  
4934 precipitated in different forms with different reagents. Technetium (VII) is primarily present in  
4935 solution as the pertechnetate anion, and macro quantities are precipitated with large cations such as  
4936 thallium ( $\text{Tl}^{+1}$ ), silver ( $\text{Ag}^{+1}$ ), cesium ( $\text{Cs}^{+1}$ ), and tetraphenylarsonium [ $(\text{C}_6\text{H}_5)_4\text{As}^{+1}$ ]. the  
4937 latter ion is the most efficient if ice-bath conditions are used. Perchtechnate is coprecipitated  
4938 without interference from molybdenum with these cations and perrhenate ( $\text{ReO}_4^{-1}$ ), perchlorate  
4939 ( $\text{ClO}_4^{-1}$ ), periodate ( $\text{IO}_4^{-1}$ ), and tetrafluoroborate ( $\text{BF}_4^{-1}$ ). The salt consisting of tetraphenylar-  
4940 senium and the perrhenate forms a coprecipitate fastest, in several seconds. Technetium (VII) can  
4941 be precipitated from solution as the heptasulfide ( $\text{Tc}_2\text{S}_7$ ) by the addition of hydrogen sulfide (or  
4942 hydrogen sulfide generating compounds such as thioacetamide and sodium thiosulfate) from 4 M  
4943 sulfuric acid. Since many other transition metals often associated with technetium also form  
4944 insoluble compounds with sulfide, the method is primarily used to concentrate technetium.

4945 Technetium (IV) is carried by ferric hydroxide. The method can be used to separate technetium  
4946 from rhenium. The precipitate is solubilized and oxidized with concentrated nitric acid, and iron  
4947 is removed by precipitation with aqueous ammonia. Technetium is also coprecipitated as the  
4948 hexachlorotechnate (IV) ( $\text{TcCl}_6^{-2}$ ) with thallium and  $\alpha,\alpha'$ -dipyridylhexachlororhenate (IV).

4949 Technetium (VI) (probably as  $\text{TcO}_{4.2}$ ) is carried quantitatively by molybdenum 8-hydroxyquino-  
4950 late and by silver or lead molybdate. Technetium (III) is carried quantitatively by iron or zinc  
4951 hydroxide and the sulfide, hydroxide, and 8-hydroxyquinolate of molybdenum.

4952 SOLVENT EXTRACTION. Technetium, primarily in the Tc (VII) state (pertechnetate) can be  
4953 isolated by extraction with organic solvents, but the principal disadvantage of all extraction  
4954 systems is the inevitable introduction of organic material that might reduce the pertechnetate  
4955 anion and cause difficulties in subsequent analytical steps. The pertechnetate ion is extracted  
4956 with pyridine from a 4 M sodium hydroxide solution, but perrhenate and permanganate ions are  
4957 also extracted. The anion also extracts into chloroform in the presence of the tetraphenyl-  
4958 arsonium ion as tetraphenylarsonium pertechnetate. Extraction is more favorable from neutral or  
4959 basic sulfate solutions than chloride solutions. Perrhenate and perchlorate are also extracted but  
4960 molybdenum does not interfere. Small amounts of hydrogen peroxide in the extraction mixture to  
4961 prevent reduction of pertechnetate. Technetium is back-extracted into 0.2 M perchloric acid or 12  
4962 M sulfuric acid. Other organic solvents are have also been used to extract pertechnetate from acid  
4963 solutions, including alcohols, ketones, and tributyl phosphate. Ketones and cyclic amines are  
4964 more effective for extraction form basic solutions. Tertiary amines and quaternary ammonium  
4965 salts are more effective extracting agents than alcohols, ketones, and tributyl phosphate. Back  
4966 extraction is accomplished several ways, depending on the extraction system. A change in pH,  
4967 displacement by another anion such as perchlorate, nitrate, or bisulfate, or addition of a nonpolar  
4968 solvent to an extraction system consisting of an oxygen-containing solvent.

4969 A recent extraction method has been used successfully for extraction chromatography and  
4970 extractive filtration. A column material consisting of trioctyl and tridecyl methyl ammonium  
4971 chlorides impregnated in an inert apolar polymeric matrix is used to separate <sup>99</sup>Tc by loading the  
4972 radionuclide as the pertechnetate ion from a 0.1 M nitric acid solution. It is stripped off the  
4973 column with 12 M nitric acid. Alternatively, the extraction material is used in a filter disc, and  
4974 the samples containing <sup>99</sup>Tc are filtered from water at pH 2 and rinsed with 0.01 M nitric acid.  
4975 Technetium is collected on the disc.

4976 Lower oxidation states of technetium are possible. The thiocyanate complexes of technetium (V)  
4977 is soluble in alcohols, ethers, ketones, and trioctylphosphine oxide or trioctylamine hydrochloride  
4978 in cyclohexane or 1,2-dichloroethane. Technetium (IV), as  $TcCl_6^{-2}$ , extracts into chloroform in  
4979 the presence of high concentrations of tetraphenylarsonium ion. Pertechnate and perrhenate are  
4980 both extracted from alkaline solution by hexone (methyl isobutyl ketone), but reduction of  
4981 technetium to the IV state with hydrazine or hydroxylamine results in the extraction of perrhenate  
4982 only.

4983 ION-EXCHANGE CHROMATOGRAPHY. Ion-exchange chromatography is primarily performed with  
4984 technetium as the pertechnate anion. Technetium does not exchange on cation resins, so  
4985 technetium is rapidly separated from other cations on these columns. In contrast, it is strongly  
4986 absorbed on strong anion exchangers and is eluted with anions that have a greater affinity for the

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4987 resin. Technetium and molybdenum are separated using ammonium thiocyanate as the eluent. A  
4988 good separation of pertechnetate and molybdate has been achieved on an anion-exchange resin in  
4989 the phosphate form where the molybdate is preferentially absorbed. Good separation of  
4990 pertechnetate and perrhenate are obtained with perchlorate as the eluent.

4991 VOLATILIZATION. The volatility of technetium heptoxide allows the co-distillation of technetium  
4992 with acids. Co-distillation from perchloric acid gives good yields, but only a partial separation  
4993 from rhenium is achieved. Molybdenum is also carried unless complexed by phosphoric acid.  
4994 Separation from rhenium can be achieved from sulfuric acid, but yields of technetium are can be  
4995 very poor because of its reduction by trace impurities in the acid. Much more reproducible results  
4996 can be obtained in the presence of an oxidizing agent, but ruthenium tetroxide ( $\text{RuO}_4$ ) also  
4997 distills under these conditions. It can be removed, however, by precipitation as ruthenium dioxide  
4998  $\text{RuO}_2$ . In distillation from sulfuric acid-water mixtures, technetium distills in the low-boiling  
4999 point aqueous fraction, probably as pertechnetic acid. Technetium and rhenium are separated  
5000 from sulfuric-hydrochloric acid mixtures; pertechnetate is reduced to non-volatile Tc (IV) and  
5001 remains in the acid solution. Technetium heptoxide can be separated from molybdenum trioxide  
5002 by fractional sublimation at temperatures  $\geq 300$  °C.

5003 ELECTRODEPOSITION. Technetium can be electrodeposited as its dioxide ( $\text{TcO}_2$ ) from 2 M  
5004 sodium hydroxide. The metal is partially separated from molybdenum and rhenium, but  
5005 deposition only occurs from low technetium concentrations. Carrier-free  $^{95}\text{Tc}$  and  $^{96}\text{Tc}$  have been  
5006 electrolyzed on a platinum electrode from dilute sulfuric acid. Optimum electroplating of  
5007 technetium has been achieved at pH 5.5 in the presence of very dilute fluoride ion. Yields were  
5008 better with a copper electrode instead of platinum—about 90 percent was collected in two hours.  
5009 Yields of 98-99 percent were achieved for platinum electrodes at pH 2-5 when the plating time of  
5010 up to 20 hours was used. In 2 M sulfuric acid containing traces of fluoride, metallic technetium  
5011 instead of the dioxide is deposited on the electrode.

### 5012 Methods of Analysis

5013  $^{99}\text{Tc}$  is analyzed by ICP-MS or from its beta emission. No gamma rays are emitted by this  
5014 radionuclide. For ICP-MS analysis, technetium is stripped from an extraction chromatography  
5015 resin and measured by the spectral system. The results should be corrected for interference by  
5016  $^{99}\text{Ru}$ , if present. For beta analysis, technetium can be electrodeposited on a platinum disc and beta  
5017 counted. Alternatively, it is collected by extraction-chromatography techniques. The resin from a  
5018 column or the disc from a filtration system is placed in a liquid scintillation vial and counted.  
5019  $^{99\text{m}}\text{Tc}$  ( $t_{1/2}=6.0\text{h}$ ), measured by gamma-ray spectrometry, can be used as a tracer for measuring the  
5020 chemical yield of  $^{99}\text{Tc}$  procedures. Beta emission from the tracer should then be subtracted from

5021 the total beta count when measuring  $^{99}\text{Tc}$ . Alternatively, samples are counted immediately after  
5022 isolation and concentration of technetium to determine the chemical recovery, then the  $^{99\text{m}}\text{Tc}$  is  
5023 allowed to decay before analysis of the  $^{99}\text{Tc}$ . A widely used medical application is the technetium  
5024 generator.  $^{98}\text{Mo}$  is neutron irradiated and chemically oxidized to  $^{99}\text{MoO}_4^{2-}$ . This solution is ion  
5025 exchange onto an acid-washed alumina column. After about 1.25 days, the activity of  $^{99\text{m}}\text{Tc}$  has  
5026 grown-in to its maximum concentration. The  $^{99}\text{Tc}$  is eluted with a 0.9% solution of NaCl, while  
5027 the  $^{99}\text{Mo}$  remains on the column. The column may have its  $^{99\text{m}}\text{Tc}$  removed after another 1.25  
5028 days, but at a slightly smaller concentration. The  $^{99\text{m}}\text{Tc}$  thus separated is carrier free. This process  
5029 historically was referred to as “milking,” and the alumina column was call the “cow.”

5030           Compiled from: Anders, 1960; CRC, 1998-99; Choppin et al., 1995; Cobble, 1964;  
5031           Considine and Considine, 1983; Coomber, 1975; Cotton and Wilkinson, 1988; DOE, 1990  
5032           and 1997, 1995, 1997; Ehmann and Vance, 1991; Fried, 1995; Greenwood and Earnshaw,  
5033           1984; Hassinsky and Adloff, 1965; Kleinberg et al., 1960; Lindsay, 1988; SCA, 2001; and  
5034           Wahl and Bonner, 1951.

#### 5035 14.10.9.9 Thorium

5036 Thorium, with an atomic number of 90, is the second member in the series of actinide elements.  
5037 It is one of only three of the actinides—thorium, protactinium, and uranium—that occur in nature  
5038 in quantities sufficient for practical extraction. In solution, in all minerals, and in virtually all  
5039 compounds, thorium exists in the +4 oxidation state; it is the only actinide exclusively in the +4  
5040 state in solution.

#### 5041 Isotopes

5042 There are 24 isotopes of thorium ranging inclusively from  $^{213}\text{Th}$  to  $^{236}\text{Th}$ ; all are radioactive.  
5043  $^{232}\text{Th}$ , the parent nuclide in the natural decay series, represents virtually 100 percent of the  
5044 thorium isotopes in nature, but there are a trace amounts of  $^{227}\text{Th}$ ,  $^{228}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{231}\text{Th}$ , and  $^{234}\text{Th}$ .  
5045 The remaining isotopes are artifacts. The most important environmental contaminants are  $^{232}\text{Th}$   
5046 and  $^{230}\text{Th}$ , (a member of the  $^{238}\text{U}$  decay series). They have half-lives of  $1.41 \times 10^{10}$  years and  
5047 75,400 years, respectively.

#### 5048 Occurrence and Uses

5049 Thorium is widely but sparsely dispersed in the Earth’s crust. At an average concentration of  
5050 approximately 10 ppm, it is over three times as abundant as uranium. In the ocean and rivers,  
5051 however, its concentration is about one-thousandth that of uranium (about  $10^{-8}$  g/L) because its

5052 compounds are much less soluble under environmental conditions. There are six minerals whose  
5053 essential element is thorium; thorite (uranothorite) and thorianite are common examples. Several  
5054 lanthanum and zirconium minerals are also thorium-bearing minerals; examples include  
5055 monazite sand and uraninite. In each mineral, thorium is present as its oxide, thorium dioxide  
5056 (ThO<sub>2</sub>). Monazite sand is the most common commercial mineral, but thorite is also a source of  
5057 thorium.

5058 Thorium is extracted from its minerals with hot sulfuric acid or hot concentrated alkali,  
5059 converted into thorium nitrate [Th(NO<sub>3</sub>)<sub>4</sub>] (its chief commercial compound), extracted with  
5060 organic solvents (commonly kerosene containing tributylphosphate), stripped from the organic  
5061 phase by alkali solutions, and crystallized as thorium nitrate or precipitated with oxalate. The  
5062 metal can be produced by electrodeposition from the chloride or fluoride dissolved in fused alkali  
5063 halides or by thermoreduction of thorium compounds by calcium (1,000–1,200 °C). Thorium can  
5064 also be produced as a by-product in the production of other valuable metals such as nickel,  
5065 uranium, and zirconium, in addition to the lanthanides. Unextracted minerals or partially  
5066 extracted mill tailings represent some forms of thorium contaminants found in the environment.  
5067 Very insoluble forms of thorium hydroxide [Th(OH)<sub>4</sub>] are other common species found.

5068 Metallic thorium has been used as an alloy in the magnesium industry and as a deoxidant for  
5069 molybdenum, iron, and other metals. Because of its high density, chemical reactivity, poor  
5070 mechanical properties, and relatively high cost, it is not used as a structural material. Thorium  
5071 dioxide is a highly refractory material with the highest melting point among the oxides, 3,390  
5072 °C. It has been used in the production of gas mantles, to prevent crystallization of tungsten in  
5073 filaments, as furnace linings, in nickel alloys to improve corrosion resistance, and as a catalyst in  
5074 the conversion of methanol to formaldehyde. <sup>232</sup>Th is a fuel in breeder reactors. The radionuclide  
5075 absorbs slow neutrons, and with the consecutive emission of two beta particles, it decays to <sup>233</sup>U,  
5076 a fissionable isotope of uranium with a half-life of 159,000 years.

#### 5077 Solubility of Compounds

5078 Thorium exists in solution as a highly charged ion and undergoes extensive interaction with  
5079 water and with many anions. Few of the compounds are water soluble; soluble thorium  
5080 compounds include the nitrate [Th(NO<sub>3</sub>)<sub>4</sub>], sulfate [Th(SO<sub>4</sub>)<sub>2</sub>], chloride (ThCl<sub>4</sub>), and perchlorate  
5081 [Th(ClO<sub>4</sub>)<sub>4</sub>]. Many compounds are insoluble in water and are used in the precipitation of thorium  
5082 from solution, including the hydroxide [Th(OH)<sub>4</sub>], fluoride (ThF<sub>4</sub>), iodate [Th(IO<sub>3</sub>)<sub>4</sub>], oxalate  
5083 [Th(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>], phosphate [Th<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>], sulfite [Th(SO<sub>3</sub>)<sub>2</sub>], dichromate [Th(Cr<sub>2</sub>O<sub>7</sub>)<sub>2</sub>], potassium  
5084 hexafluorothorionate [K<sub>2</sub>ThF<sub>6</sub>], thorium ferrocyanide (II) [ThFe(CN)<sub>6</sub>], and thorium peroxide  
5085 sulfate [Th(OO)<sub>2</sub>SO<sub>4</sub>].

5086 The thorium ion forms many complex ions, chelates, and solvated species that are soluble in  
5087 organic solvents. This property is the basis of many procedures for the separation and purification  
5088 of thorium (see below). For example, certain ions, such as nitrate and sulfate, form large  
5089 unsolvated complex ions with thorium that are soluble in organic solvents. Chelates of 1,3-  
5090 diketones, such as acetylacetone (acac) and 2-thenoyltrifluoroacetone (TTA), form neutral  
5091 molecular chelates with the thorium ion that are soluble. In addition, many neutral organic  
5092 compounds have strong solvating properties for thorium, bonding to the thorium ion in much the  
5093 same way water solvates the ion at low pH. Tributylphosphate (TBP), diethyl ether, methyl ethyl  
5094 ketone, mesityl oxide, and monoalkyl and dialkyl phosphates are examples of such compounds.

5095 Review of Properties

5096 Thorium is the first member of the actinide series of elements that includes actinium (Ac),  
5097 uranium, and the transuranium elements. Thorium is a bright, silver-white metal with a density  
5098 above 11 g/cm<sup>3</sup>. It tarnishes in air, forming a dark gray oxide coating. The massive metal is  
5099 stable, but in finely divided form and as a thin ribbon it is pyrophoric and forms thorium oxide  
5100 (ThO<sub>2</sub>). Thorium metal dissolves in hydrochloric acid, is made passive by nitric acid, but is not  
5101 affected by alkali. It is attacked by hot water and steam to form the oxide coating and hydrogen,  
5102 but its reactions with water are complicated by the presence of oxygen. Thorium has four valence  
5103 electrons (6d<sup>2</sup>7s<sup>2</sup>). Under laboratory conditions, chlorides, bromides, and iodides of the bi- and  
5104 trivalent state have been prepared. In aqueous solution and in most compounds, including all  
5105 those found in nature, thorium exists only in the +4 oxidation state; its compounds are colorless  
5106 in solution unless the anion provides a color. Thorium forms many inorganic compounds in acid  
5107 solution.

5108 Solution Chemistry

5109 Because the only oxidation state of thorium in solution is the +4 state, its chemistry is not  
5110 complicated by oxidation-reductions reactions that might produce alternate species in solution.  
5111 With the +4 charge and corresponding charge-to-radius ratio of 4.0, however, thorium forms very  
5112 stable complex ions with halides, oxygen-containing ligands, and chelating agents. Although  
5113 Th<sup>+4</sup> is large (0.99 Å; 0.099 nm; 99 pm) relative to other +4 ions (Ti, Zr, Hf, Ce) and therefore  
5114 more resistant to hydrolysis, as a highly charged ion, it hydrolyzes extensively in aqueous  
5115 solutions above pH 3 and tends to behave more like a colloid than a true solution. The  
5116 concentration of Th<sup>+4</sup> is negligible under those conditions. Below pH 3, however, the  
5117 uncomplexed ion is stable as the hydrated ion, Th(H<sub>2</sub>O)<sub>8 or 9</sub><sup>+4</sup>.

5118 COMPLEXATION. Thorium has a strong tendency to form complex ions in solution. The presence  
5119 of HF forms very stable complex ions, for example, with one, two, or three ligands:



5123 These complex ions represent the predominant species in solutions containing HF. Stable  
5124 complex ions also form with oxygen-containing ligands such as nitrate, chlorate, sulfate,  
5125 bisulfate, iodate, carbonate, phosphate, most carboxylate anions, and chelate anions. Some  
5126 chelating agents such as salicylate, acetylacetonate (acac), theonyltrifluoroacetate (TTA), and  
5127 cupferron form complexes that are more soluble in organic solvents. This property is the basis of  
5128 several radiochemical isolation methods for thorium. Through the formation of soluble complex  
5129 ions, chelating agents found in some industrial wastewater or natural water samples will interfere  
5130 to varying degrees with the isolation of thorium by ferric hydroxide [Fe(OH)<sub>3</sub>] coprecipitation.  
5131 Alternative isolation methods should be used, such as coprecipitation from an acidic solution  
5132 with an alternative reagent. Protonation of the anionic form of chelates with acid renders them  
5133 useless as chelating agents. Other complexing agents also interfere with precipitation by the  
5134 formation of soluble ions. Thorium, for example, does not precipitate with oxalate in the  
5135 presence of carbonate ions. A procedure for separating thorium from rare-earth ions takes  
5136 advantage of the formation of a soluble thorium-EDTA complex that inhibits thorium  
5137 precipitation when the rare-earth ions are precipitated with phosphate. The presence of high  
5138 concentrations of other complexing agents such as phosphate, chloride, and other anions found in  
5139 some samples takes thorium into a completely exchangeable form when it is solubilized in high-  
5140 concentration nitric acid.

5141 HYDROLYSIS. Beginning at pH 3, thorium ions undergo extensive hydrolysis to form monomeric  
5142 and polymeric complexes in solution, leaving little (approximately  $5 \times 10^{-6}$  M) Th<sup>+4</sup> in a saturated  
5143 solution at pH 3. Tracer solutions containing <sup>234</sup>Th can be added at pH 2 to allow equilibration  
5144 because it is not likely to occur if part of the thorium is hydrolyzed and bound in polymeric  
5145 forms.

5146 The hydrolysis process is complex, depending on the pH of the solution and its ionic strength.  
5147 Several species have been proposed: three are polynuclear species, Th<sub>2</sub>(OH)<sub>2</sub><sup>+6</sup>, Th<sub>4</sub>(OH)<sub>8</sub><sup>+8</sup>, and  
5148 Th<sub>6</sub>(OH)<sub>15</sub><sup>+9</sup>; and two are monomeric species, Th(OH)<sup>+3</sup> and Th(OH)<sub>2</sub><sup>+2</sup>. The monomeric species  
5149 are of minor importance except in extremely dilute solutions, but they become more important as  
5150 the temperature increases. The presence of chloride and nitrate ion diminishes hydrolysis,  
5151 because the formation of corresponding complex ions markedly suppresses the process.

5152 Hydrolysis increases with increasing hydroxide concentration (pH), and eventually polymeriza-  
5153 tion of the species begins. At a pH of about 5, irreversible hydrolysis produces an amorphous  
5154 precipitate of thorium hydroxide, a polymer that might contain more than 100 thorium atoms.  
5155 Just before precipitation, polymerization slows and equilibration might take weeks or months to  
5156 obtain.

5157 Routine fuming of a sample containing organic material with nitric acid is recommended after  
5158 addition of tracer, but before separation of thorium as a hydroxide precipitate because there is  
5159 evidence for lack of exchange between added tracer and isotope already in solution. Complexing  
5160 with organic substances in the initial solution or existence of thorium in solution as some  
5161 polymeric ion have been suggested as the cause.

5162 ADSORPTION. The insoluble hydroxide that forms in solution above pH 3 has a tendency to  
5163 coagulate with hydrated oxides such as ferric oxide. The high charge of the thorium cation (+4),  
5164 high charge-to-radius ratio, and tendency to hydrolyze all contribute to the ability of thorium to  
5165 adsorb on surfaces by ion-exchange mechanisms or chemical adsorption mechanisms. These  
5166 adsorption properties greatly affect the interaction of thorium with ion-exchange resins and  
5167 environmental media such as soil.

#### 5168 Dissolution of Samples

5169 Thorium samples are ignited first to remove organic materials. Most compounds will decompose  
5170 when sintered with sodium peroxide ( $\text{Na}_2\text{O}_2$ ), and most thorium minerals will yield to alternate  
5171 sodium peroxide sintering and potassium pyrosulfate ( $\text{K}_2\text{S}_2\text{O}_7$ ) fusion. It is often necessary to  
5172 recover thorium from hydrolysis products produced by these processes. The hydrolysis products  
5173 are treated with hydrofluoric acid, and thorium is recovered as the insoluble fluoride. Rock  
5174 samples are often dissolved in hydrofluoric acid containing either nitric acid or perchloric acid.  
5175 Monazite is dissolved by prolonged sintering or with fuming perchloric or sulfuric acid. Thorium  
5176 alloys are dissolved in two steps, first with aqua regia (nitric and hydrochloric acid mixture)  
5177 followed by fusion with potassium pyrosulfate. Thorium targets are dissolved in concentrated  
5178 nitric acid containing hydrofluoric acid, mantles in nitric or sulfuric acid, and tungsten filaments  
5179 with aqua regia or perchloric acid.

#### 5180 Separation Methods

5181 PRECIPITATION AND COPRECIPITATION. Precipitation and coprecipitation are used to separate and  
5182 collect thorium from aqueous solutions either for further treatment in an analytical scheme or for  
5183 preparation of a sample for counting. Formation of insoluble salts is used to precipitate thorium

5184 from solution; examples include the hydroxide, peroxide, fluoride, iodate, oxalate, and  
5185 phosphate, among others. Tracer quantities of thorium are commonly coprecipitated with  
5186 lanthanum fluoride (LaF<sub>3</sub>), neodymium fluoride (NdF<sub>3</sub>), and cerium fluoride (CeF<sub>3</sub>) in separation  
5187 schemes and to prepare samples for alpha counting. Tracer quantities are also carried with  
5188 calcium oxalate [Ca(C<sub>2</sub>O<sub>4</sub>)], ferric hydroxide [Fe(OH)<sub>3</sub>], zirconium iodate (ZrIO<sub>4</sub>), zirconium  
5189 phosphate (Zr<sub>3</sub>PO<sub>4</sub>), and barium sulfate (BaSO<sub>4</sub>).

5190 ION EXCHANGE. The highly charged thorium cation is strongly adsorbed onto cation exchangers  
5191 and is more difficult to elute than most other ions. Its strong adsorption property makes it  
5192 possible to remove trace quantities of thorium from a large volume of solution onto small  
5193 amounts of ion-exchange resin. Washing the resin with mineral acids of various concentrations  
5194 separates thorium from less strongly bound cations that elute from the resin. For example, Th<sup>+4</sup>  
5195 remains bonded at all hydrochloric concentrations, allowing other cations to be eluted at different  
5196 concentrations of acid. Thorium is eluted by complexing agents such as citrate, lactate, fluoride,  
5197 carbonate, sulfate, or oxalate that reduce the net charge of the absorbing species, causing reversal  
5198 of the adsorption process.

5199 Anion exchangers are useful for separating thorium, but the contrasting behavior of thorium with  
5200 the resin depends on whether hydrochloric or nitric acid is used as an eluent. In hydrochloric  
5201 acid, several metal ions, unlike thorium, form negative complexes that can be readily removed  
5202 from a thorium solution by adsorption onto the anionic exchanger. Thorium forms positively  
5203 charged chlorocation complexes or neutral thorium chloride (ThCl<sub>4</sub>) in the acid and is not  
5204 adsorbed by the resin at any hydrochloric acid concentration. In contrast, thorium forms anionic  
5205 complexes in nitric acid solution that adsorb onto the exchanger over a wide range of nitric acid  
5206 concentrations, reaching a maximum affinity near 7 M nitric acid. Behavior in nitric acid solution  
5207 is the basis for a number of important radiochemical separations of thorium from rare earths,  
5208 uranium, and other elements.

5209 ELECTRODEPOSITION. Thorium separated from other actinides by chemical methods can be  
5210 electrodeposited for alpha counting from a dilute solution of ammonium sulfate adjusted to a pH  
5211 of 2. The hydrous oxide of thorium is deposited in one hour on a highly polished platinum disc  
5212 serving as the cathode of an electrolytic cell. The anode is a platinum-iridium alloy.

5213 SOLVENT EXTRACTION. Many complexes and some compounds of thorium can be extracted from  
5214 aqueous solutions into a variety of organic solvents. The TTA ( $\alpha$ -theonyltrifluoroacetone)  
5215 complex of metals is widely used in radiochemistry for the separation of ions. Thorium can be  
5216 separated from most alkali metal, alkaline earth, and rare earth metals after the complex is  
5217

5218 quantitatively extracted into benzene above pH 1. Backwashing the organic solution with dilute  
5219 acid leaves the more soluble ions in benzene.

5220 Extraction of nitrates and chlorides of thorium into organic solvents from the respective acid  
5221 solutions is widely used for isolation and purification of the element. One of the most common  
5222 processes is the extraction of thorium nitrate from a nitric acid solution with TBP (triisobutyl-  
5223 phosphate). TBP is usually diluted with an inert solvent such as ether or kerosene to reduce the  
5224 viscosity of the mixture. Dilution reduces the extraction effectiveness of the mixture, but the  
5225 solubility of many contaminating ions is greatly reduced, increasing the effectiveness of the  
5226 separation when the thorium is recovered by backwashing.

5227 Long-chain amine salts have been very effective in carrying thorium in laboratory and industrial  
5228 extraction process using kerosene. Complex sulfate anions of thorium are formed in sulfuric acid  
5229 that act as the counter ion to the protonated quaternary amine cation. They accompany the  
5230 organic salt into the organic phase.

5231 In recent years, solvent extraction chromatography procedures have been developed to separate  
5232 thorium. These procedures use extraction chromatography resins that consist of extractant  
5233 materials such as CMPO in TBP or DPPP (dipentylpentylphosphonate), also called DAAP  
5234 (diamylamylphosphonate), absorbed onto an inert polymeric material. They are used in a column,  
5235 rather than in the traditional batch mode, and provide a rapid efficient method of separating the  
5236 radionuclide with the elimination of large volumes of organic waste.

#### 5237 Methods of Analysis

5238 Chemical procedures are used for the analysis of macroscopic quantities of thorium in solution  
5239 after it has been separated by precipitation, ion exchange, extraction, and/or extraction chroma-  
5240 tography from interfering ions. Gravimetric determination generally follows precipitation as the  
5241 oxalate that is calcined to the oxide ( $\text{ThO}_2$ ). Numerous volumetric analyses employ EDTA as the  
5242 titrant. In the most common spectrometric method of analysis, thorin, a complex organoarsenic  
5243 acid forms a colored complex with thorium that is measured in the visible spectrum.

5244 Trace quantities of thorium are measured by alpha spectrometry after chemical separation from  
5245 interfering radionuclides.  $^{227}\text{Th}$ ,  $^{228}\text{Th}$ ,  $^{230}\text{Th}$ , and  $^{232}\text{Th}$  are determined by the measurement of  
5246 their respective spectral peaks (energies), using  $^{234}\text{Th}$  as a tracer to determine the chemical yield  
5247 of the procedure. The activity of the tracer is determined by beta counting in a proportional  
5248 counter.  $^{234}\text{Th}$  also emits gamma radiation that can be detected by gamma spectrometry; however,  
5249 the peak can not be measured accurately because of interfering peaks of other gamma-emitting

5250 radionuclides.  $^{229}\text{Th}$  is sometimes used as a tracer to determine the chemical yield of the alpha  
5251 spectrometric procedure, but it produces considerable recoil that might contaminate the detector.

5252           Compiled from: Ahrland, 1986; Baes and Mesmer, 1976; Cotton, 1991; Cotton and  
5253           Wilkinson, 1988; DOE, 1990 and 1997, 1997; EPA, 1980 and 1984; Greenwood, 1984;  
5254           Grimaldi, 1961; Hassinsky and Adloff, 1965; Hyde, 1960; Katzin, 1986; Lindsey, 1988.

#### 5255   14.10.9.10 Tritium

5256   Unlike the elements reviewed in this section, tritium the only radionuclide of the element  
5257   hydrogen. It contains two neutrons and is represented by the symbols  $^3\text{H}$ ,  $^3\text{T}$ , or simply, T. The  
5258   atom contains only one valence electron so its common oxidation state, besides zero, is +1,  
5259   although it can exist in the -1 state as a metal hydride.

#### 5260   Occurrence and Uses

5261   Tritium is found wherever stable hydrogen is found, with and without the other isotopes of the  
5262   element (hydrogen and deuterium)—as molecular hydrogen (HT, DT,  $\text{T}_2$ ), water (HTO, DTO,  
5263    $\text{T}_2\text{O}$ ), and inorganic and organic compounds, hydrides and hydrocarbons, respectively, for  
5264   example. About 99 percent of the radionuclide in nature from any source is in the form of HTO.  
5265   Natural processes account for approximately one T atom per  $10^{18}$  hydrogen atoms. The source of  
5266   some natural tritium is ejection from the sun, but the primary source is from bombardment of  $^{14}\text{N}$   
5267   with cosmic neutrons in the upper atmosphere:



5269   Most tritium from this source appears as HTO.

5270   Tritium is produced in laboratory and industrial processes by nuclear reactions such as:



5272   For large-scale production of tritium,  $^6\text{Li}$  alloyed with magnesium or aluminum is the target of  
5273   neutrons:

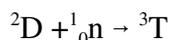


5275 The radionuclide is retained in the alloy until released by acid dissolution of the target. Large  
5276 quantities are handled as HT or HTO. HTO is formed from HT when it is exposed to oxygen or  
5277 water vapor. A convenient way to store tritium is as the hydride of uranium (UT<sub>3</sub>). It is formed by  
5278 reacting the gas with finely divided uranium and is released by heating the compound above 400  
5279 °C.

5280 Tritium is also produced in nuclear reactors that contain water or heavy water from the neutron  
5281 bombardment of deuterium:

5282

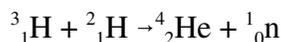
5283



5284 Most tritium (>99%) in reactors is formed from the fission process as a ternary particle.

5285 The main use for tritium is in fission bombs to boost their yield and in thermonuclear weapons,  
5286 the hydrogen bomb. Tritium bombarded with high-energy deuterons undergoes fusion to form  
5287 helium and releasing neutrons:

5288



5289 A tremendous amount of energy is released during the nuclear reaction, much more than the  
5290 energy of the bombarding particle. Fusion research on controlled thermonuclear reactions should  
5291 lead to an energy source for electrical generation.

5292 Tritium absorbed on metals are a source of neutrons when bombarded with deuterons. Mixed  
5293 with zinc sulfide, it produces radioluminescence that is used in luminescent paint and on watch  
5294 dials. Gaseous tritium in the presence of zinc sulfide produces a small, permanent light source  
5295 found in rifle sights and exit signs. Tritium is also a good tracer since it does not emit gamma  
5296 radiation. Hydrological studies with HTO is used to trace geological water and the movement of  
5297 glaciers. It is also used as a tracer for hydrogen in chemical studies and biological research. In  
5298 medicine, it is used for diagnosis and radiotreatment.

### 5299 Review of Properties

5300 Tritium decays with a half-life of 12.3 y by emission of a low-energy beta particle to form <sup>3</sup>He,  
5301 and no gamma radiation is released. The range of the beta particle is low, 6 mm in air and 0.005  
5302 mm in water or soft tissue.

5303

5304 The physical and chemical properties of tritium are somewhat different than hydrogen or  
5305 deuterium because of their mass differences (isotope effects). Tritium is approximately twice as

5306 heavy as deuterium and three times heavier than hydrogen, and the isotope effect can be large for  
5307 mass differences of these magnitudes. In its simple molecular form, tritium exists primarily as T<sub>2</sub>  
5308 or DT. The oxide form is HTO, DTO, or T<sub>2</sub>O, with higher molecular weights than water (H<sub>2</sub>O).  
5309 Thus molecules of tritiated water are heavier, and any process such as evaporation or distillation  
5310 that produces a phase transition results in isotopic fractionation and enrichment of tritium in  
5311 water. In a mixture of the oxides, various mixed isotopic water species are generally also present  
5312 because of exchange reactions: in any mixture of H<sub>2</sub>O, D<sub>2</sub>O, and T<sub>2</sub>O, HTO and DTO are  
5313 found. Molecules of HTO are more stable than H<sub>2</sub>O or HDO and are not as easily decomposed by  
5314 electrolysis, to form hydrogen or oxygen. Electrolysis of a water sample to about five percent of  
5315 its original volume, therefore, concentrates tritium by retaining approximately 80 percent of the  
5316 tritium from the initial volume. Reaction rates of chemical bonds containing tritium are slower  
5317 because of the isotope effect than those of hydrogen. The rates can be as small as 1:64 (T:H), and  
5318 these differences should be considered when interpreting tracer studies of reaction mechanisms.  
5319 Chemical isotope effects are large in some biological systems. Some algae and bacteria  
5320 selectively exchange hydrogen isotopes, and the preference is tritium over deuterium over  
5321 hydrogen. Enrichment of tritium can be about 2.5.

5322 Tritium can be introduced into organic compounds by exposing T<sub>2</sub> to the compound for a few  
5323 days or weeks, irradiation of the compound and a lithium salt with neutrons (recoil labeling), or it  
5324 can be selectively introduced into a molecule by chemical synthesis using a molecular tritium  
5325 source such as HTO. Beta radiation causes exchange reactions between hydrogen atoms in the  
5326 compound and tritium and migration of the isotope within the molecule. Phenol (C<sub>6</sub>H<sub>5</sub>OH), for  
5327 example, labeled with tritium on the oxygen atom (C<sub>6</sub>H<sub>5</sub>OT) will become C<sub>6</sub>H<sub>4</sub>TOH and  
5328 C<sub>6</sub>H<sub>4</sub>TOT. When tritium samples are stored in containers made from organic polymers such as  
5329 polyethylene, the container will adsorb tritium, resulting in a decrease in the concentration of  
5330 tritium in the sample. Eventually, the tritium atoms will migrate to the outer surface of the  
5331 container, and tritium will be lost to the environment. Catalytic exchange also occurs in tritiated  
5332 solutions or solutions containing T<sub>2</sub> gas. Exchange is very rapid with organic compounds when  
5333 H<sup>+1</sup> or OH<sup>-1</sup> ions or if a hydrogen-transfer agent such as Pt or Pd is present.

5334 Tritium as HT or HTO will absorb on most metallic surfaces. Penetration at room temperature is  
5335 very slow, and the radionuclide remains close to the surface. In the form of HTO, it can be  
5336 removed with water, or by hydrogen gas in the form of HT. Heating aids the removal. When  
5337 tritium is absorbed at elevated temperatures, it penetrates deeper into the surface. Adsorption  
5338 under these conditions will result in enough penetration to cause structural damage to the metal,  
5339 especially if the process continues for extended periods. Hydrogenous material such as rubber  
5340 and plastics will also absorb tritium. It will penetrate into the material, and hydrogenous  
5341 materials are readily contaminated deep into the material, and it is impossible to completely

5342 remove the tritium. Highly contaminated metal or plastic surfaces can release some of the loosely  
5343 bound tritium immediately after exposure in a process called outgassing.

5344 Pure T<sub>2</sub>O can be prepared by oxidation of tritium gas with hot copper(II) oxide or direct  
5345 combination of the gas with oxygen in the presence of an electrical spark. It is never used for  
5346 chemical or biological processes because one milliliter contains 2,650 curies. The liquid is self-  
5347 luminescent, undergoes rapid self-radiolysis, and considerable radiation damage is done to  
5348 dissolved species. For the same reason, very few compounds of pure tritium have ever been  
5349 prepared or studied.

5350 The radiotoxicity of tritium is rated medium. Tritium is not a hazard outside the body. Gamma  
5351 radiation is not released by its decay. The beta emission is low in energy compared to most beta  
5352 emitters and readily stopped by the outer layer of skin. Only ingested tritium can be a hazard.  
5353 Exposure to tritium is primarily in the form of HT gas or HTO water vapor, although T<sub>2</sub> and T<sub>2</sub>O  
5354 may be present. Only about 0.005 percent of the activity of inhaled HT gas is incorporated into  
5355 lung tissue, and most is exhaled. Tritiated water vapor, however, is almost 100 percent absorbed  
5356 from inhalation or ingestion. In addition, tritiated water can be absorbed through the skin or  
5357 wounds. Not all gloves will prevent exposure because of the ability of tritium to be absorbed by  
5358 the gloves themselves. Tritium is found in tissue wherever hydrogen is found. The biological  
5359 half-life is about ten days, but the value varies significantly, depending on exertion rates and  
5360 fluid intake.

5361 Environmental tritium is formed in the gaseous and aqueous forms, but over 99 percent of tritium  
5362 from all sources is found in the environment after exchange with hydrogen in water in the form  
5363 of HTO. It is widely distributed in the surface waters of the earth and makes a minor contribution  
5364 to the activity of ocean water. It can also be found in laboratories and industrial sites in the form  
5365 of metal hydrides, tritiated pump oil, and tritiated gases such as methane and ammonia.

5366 Separation Methods

5367 DISTILLATION. Tritium in water samples is essentially in the form of HTO. It can be removed  
5368 quantitatively from aqueous mixtures by distillation to dryness, which also separate it from other  
5369 radionuclides. Volatile iodine radionuclides are precipitated as silver iodide before distillation, if  
5370 they are present. The aqueous solution is usually distilled, however, from a basic solution of  
5371 potassium permanganate, which will oxidize radionuclides, such as iodine and carbon, and  
5372 oxidize organic compounds that might interfere with subsequent procedures, liquid scintillation  
5373 counting, for example. Charcoal can also be added to the distillation mixture as an additional  
5374 measure to remove organic material. Contaminating tritium in soil samples can be removed by

## *Separation Techniques*

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5375 distillation from similar aqueous mixtures. All tritium in soil samples might not be recovered by  
5376 this method, however, if the tritium is tightly bound to the soil matrix. Tritium also can be  
5377 removed by distillation of an azeotrope mixture formed with toluene or cyclohexane. In some  
5378 procedures, tritium is initially separated by distillation and then concentrated (enriched) by  
5379 electrolysis in an acid or base solution. Recovery of tritium from the electrolytic cell for analysis  
5380 is accomplished by a subsequent distillation.

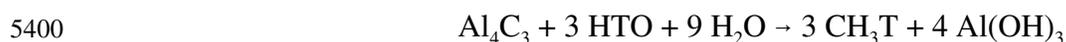
5381 DECOMPOSITION. Organically bound tritium (OBT) in vegetation, food, and tissue samples can be  
5382 removed by combustion. The sample is freeze dried (lyophilized), and the water from the process  
5383 is collected in cold traps for tritium analysis. The remaining solid is collected as a pellet, which is  
5384 burned at 700 °C in a highly purified mixture of argon and oxygen in the presence of a copper(I)  
5385 oxide (CuO) catalyst, generated on a copper screen at the temperature of the process. Water from  
5386 the combustion process, containing tritium from the pellet, and water from the freeze-drying  
5387 process is analyzed for tritium by liquid scintillation counting.

5388 Tritium in HTO can be reduced to TH by heating with metals, such as magnesium, zinc, or  
5389 calcium, and analyzed as a gas.

5390 CONVERSION TO ORGANIC COMPOUNDS. Compounds that react readily with water to produce  
5391 hydrogen derivatives can be used to isolate and recover tritium that is present in the HTO form.  
5392 Organic compounds containing magnesium (Grignard reagents) with relatively low molecular-  
5393 weights will react spontaneously with water and produce a gaseous product containing hydrogen  
5394 from the water. Tritium from HTO in a water sample will be included in the gaseous sample. It is  
5395 collected after formation by condensation in a cold trap and vaporized into a gas tube for  
5396 measurement. Grignard reagents formed from butane, acetylene, and methane can be used in this  
5397 method. Tritiated butane is produced by the following chemical reaction:



5399 Inorganic compounds can also be used to produce gaseous products:



5401 EXCHANGE. Methods to assess tritium in compounds take advantage of exchange reactions to  
5402 collect the radionuclide in a volatile substance that can be collected in a gas tube for measure-  
5403 ment. Acetone is one compound that easily exchanges tritium in an acid or base medium and is  
5404 relatively volatile.

5405 Methods of Analysis

5406 Tritium is collected primarily as HTO along with water (H<sub>2</sub> O) by distillation and then  
 5407 determined from its beta emission in a liquid scintillation system. No gamma rays are emitted.  
 5408 The distillation process is usually performed from a basic solution of potassium permanganate to  
 5409 oxidize radionuclides and organic compounds, preventing them from distilling over and  
 5410 subsequently interfering with counting. Charcoal can also be added to the distillation mixture as  
 5411 an additional measure to remove organic material. Volatile iodine radionuclides can be  
 5412 precipitated as silver iodide before distillation.

5413           Compiled from: Choppin et al., 1995; Cotton and Wilkinson, 1988; DOE, 1994; Duckworth,  
 5414           1995; Greenwood and Earnshaw, 1984; Hampel, 1968; Hassinky and Adloff, 1965; Kaplan,  
 5415           1995; Lindsay, 1988; Mitchell, 1961; Passo and Cook, 1994.

5416 14.10.9.11 Uranium

5417 Uranium, atomic number 92, is the last naturally occurring member of the actinide series and the  
 5418 precursor to the transuranic elements. Three isotopes are found in nature, and uranium was the  
 5419 active constituent in the salts whose study led to the discovery of radioactivity by Becquerel in  
 5420 1896.

5421 Isotopes

5422 There are 19 isotopes of uranium with mass numbers ranging from 222 to 242. All isotopes are  
 5423 radioactive with half-lives range ranging from microseconds to billions of years. <sup>235</sup>U (0.72%)  
 5424 and <sup>238</sup>U (99.27%) are naturally occurring as primordial uranium. <sup>234</sup>U has a natural abundance of  
 5425 0.0055%, but is present as a part of the <sup>238</sup>U decay natural decay chain. The <sup>234</sup>U that was formed  
 5426 at the time the earth was formed has long since decayed. The half-lives of these principal  
 5427 isotopes of uranium are listed below.

	<u>Isotope</u>	<u>Alpha Decay Half-Life</u>	<u>Spontaneous Fission Half-Life</u>
5428	234	2.46 x 10 <sup>5</sup> years	1.42 x 10 <sup>16</sup> years
5429	235	7.04 x 10 <sup>8</sup> years	9.80 x 10 <sup>18</sup> years
5430	238	4.48 x 10 <sup>9</sup> years	8.08 x 10 <sup>15</sup> years
5431			

## Separation Techniques

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5432 These isotopes have two different decay modes. Each decay mode has its own characteristic half-  
5433 life. As seen above the alpha decay mode is the most significant, since it has the shortest half-life  
5434 for each of these isotopes.

5435 Another isotope of uranium of significance is  $^{232}\text{U}$  (half-life 69.8 years). It is used as a tracer in  
5436 uranium analyses and is also an alpha emitter so it can be determined concurrently with the major  
5437 uranium isotopes by alpha spectrometry.

5438  $^{235}\text{U}$  and artificially produced  $^{233}\text{U}$  are fissionable material on bombardment with slow (thermal)  
5439 neutrons. Other uranium radionuclides are fissionable with fast moving neutrons, charged  
5440 particles, high-energy photons, or mesons.  $^{238}\text{U}$  and  $^{235}\text{U}$  are both parents of natural radioactive  
5441 decay series, the uranium series of  $^{238}\text{U}$  that eventually decays with alpha and beta emissions to  
5442 stable  $^{206}\text{Pb}$  and the actinium series of  $^{235}\text{U}$  that decays to  $^{207}\text{Pb}$ .

### 5443 Occurrence and Uses

5444 Naturally occurring uranium is believed to be concentrated in the earth's crust with an average  
5445 concentration of approximately 4 ppm. Granite rocks contains up to 8 ppm or more, and ocean  
5446 water contains 0.0033 ppm. Many uranium minerals have been discovered. Among the better  
5447 known are uraninite, carnotite, adavidite, pitchblende, and coffinite. The latter two minerals are  
5448 important commercial sources of uranium. It is also found in phosphate rock, lignite, and  
5449 monazite sands and is commercially available from these sources. The artificial isotope,  $^{233}\text{U}$ , is  
5450 produced from natural  $^{232}\text{Th}$  by absorption of slow neutrons to form  $^{233}\text{Th}$ , which decays by the  
5451 emission of two beta particles to  $^{233}\text{U}$ .

5452 Uranium is extracted from uranium minerals, ores, rocks, and sands by numerous chemical  
5453 extraction (leaching) processes. The extraction process is sometimes preceded by roasting the ore  
5454 to improve the processing characteristic of the material. The extraction process uses either an  
5455 acid/oxidant combination or sodium carbonate treatment, depending on the nature of the ore, to  
5456 convert the metal to a soluble form of the uranyl ion. Uranium is recovered from solution by  
5457 precipitating the uranate salt with ammonia or sodium hydroxide solution. Ammonium uranate is  
5458 know as yellow cake. The uranate salt is solubilized to give a uranyl nitrate solution that is  
5459 further purified by extraction into an organic phase to separate the salt from impurities and  
5460 subsequent stripping with water. It is precipitated as a highly purified nitrate salt that is used to  
5461 produce other uranium compounds—uranium trioxide ( $\text{UO}_3$ ) by thermal processing or uranium  
5462 dioxide ( $\text{UO}_2$ ) on reduction of the trioxide with hydrogen. Uranium tetrafluoride ( $\text{UF}_4$ ) is  
5463 prepared, in turn, from the dioxide by treatment with hydrogen fluoride. The metal is recovered

5464 by fused-salt electrolysis in molten sodium chloride-calcium chloride or reduction with more  
5465 active metals such as calcium or magnesium (Ames Process) in an inert atmosphere at 1,000 °C.

5466 Early in the twentieth century, the only use of uranium was in the production of a brown-yellow  
5467 tinted glass and glazes; it was a byproduct of the extraction of radium, which was used for  
5468 medicinal and research purposes. Since the mid-twentieth century, the most important use of  
5469 uranium is as a nuclear fuel, directly in the form of  $^{233}\text{U}$  and  $^{235}\text{U}$ , fissionable radionuclides, and  
5470 in the form of  $^{238}\text{U}$  that can be converted to fissionable  $^{239}\text{Pu}$  by thermal neutrons in breeder  
5471 reactors. Depleted uranium, uranium whose  $^{235}\text{U}$  content has been reduced to below about 0.2  
5472 percent, the majority of waste from the uranium enrichment process, is used in shielded  
5473 containers to transport radioactive materials, inertial guidance devices, gyro compasses,  
5474 counterweights for aircraft control surfaces, ballast for missile reentry vehicles, fabrication of  
5475 armor-piercing conventional weapons, and tank armor plating. Uranium metal is used as a X-ray  
5476 target for production of high-energy X-rays, the nitrate salt as a photographic toner, and the  
5477 acetate is used in analytical chemistry.

5478 Solubility of Compounds

5479 Only a small number of the numerous uranium compounds are soluble in water. Except for the  
5480 fluorides, the halides of uranium (III and IV) are soluble, as are the chloride and bromide of  
5481 uranium (V) [ $\text{UOX}_2$ ] and the fluoride, chloride, and bromide of uranium (VI) [ $\text{UO}_2\text{X}_2$ ]. Several  
5482 of the uranyl ( $\text{UO}_{2+2}$ ) salts of polyatomic anions are also soluble in water: the sulfate,  
5483 bicarbonate, acetate, thiocyanate, chromate, tungstate, and nitrate. The latter is one of the most  
5484 water-soluble uranium compounds.

5485 Review of Properties

5486 Uranium is a dense, malleable and ductile metal that exists in three allotropic forms: alpha, stable  
5487 to 688 °C where it forms the beta structure, which becomes the gamma structure at 776 °C. It is  
5488 a poor conductor of electricity. The metal absorbs gases and is used to absorb tritium. Uranium  
5489 metal tarnishes readily in an oxidation process when exposed to air. It burns when heated to 170  
5490 °C, and the finely divided metal is pyrophoric. Uranium slowly decomposes water at room  
5491 temperature, but rapidly at 100 °C. Under a flux of neutrons and other accelerated particles,  
5492 atoms of uranium are displaced from their equilibrium position in its metallic lattice. With high  
5493 temperatures and an accumulation of fission products, the metal deforms and swells, becoming  
5494 twisted, porous, and brittle. The problem can be avoided by using some of its alloys, particularly  
5495 alloys of molybdenum and aluminum.

## Separation Techniques

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5496 Uranium forms a large number of binary and ternary alloys with most metals. It also form  
5497 compounds with many metals: aluminum, bismuth, cadmium, cobalt, gallium, germanium, gold,  
5498 indium, iron, lead, magnesium, mercury, nickel, tin, titanium, zinc, and zirconium. Many binary  
5499 compounds of the nonmetals are also known: hydrides, borides, carbides, nitrides, silicides,  
5500 phosphides, halides, and oxides. Although other oxides are known, the common oxides are  $\text{UO}_2$ ,  
5501  $\text{UO}_3$ , and  $\text{U}_3\text{O}_8$ . Uranium reacts with acids to form the +4 salts and hydrogen. It is very reactive  
5502 as a strong reducing agent.

5503 Uranium compounds are toxic at high concentrations. The physiological damage occurs to  
5504 internal organs, especially the kidneys. The radioactivity of natural uranium radionuclides is not  
5505 of great concern, although it is high for some artificial isotopes. Natural uranium in the  
5506 environment is considered a relatively low hazard, however, because of its very long half-life and  
5507 low toxicity at minute concentrations.

5508 Uranium in nature is almost entirely in the IV and VI oxidation states. It occurs as the oxides,  
5509  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ , in the solid state. In ground water under oxic conditions it exists as  $\text{UO}_2^{+2}$  or  
5510 complexes of carbonate such as  $\text{UO}_2(\text{CO}_3)_3^{-4}$ . Complex formation increases its solubility under  
5511 all conditions in normal groundwater and even under fairly strong reducing conditions. The  
5512 amount associated with particulate matter is small in natural oxic waters. In some waters,  
5513 solubility may be limited, however, by formation of an uranyl silicate species. Uranium in  
5514 general is poorly absorbed on geologic media under oxic conditions, especially at moderate and  
5515 high concentrations and in the presence of high carbonate concentrations. A significant  
5516 adsorption occurs at pH above about 5 or 6 because of formation of hydrolytic complexes.  
5517 Reduction to the IV oxidation state would increase uptake in the environmental pH range.

### 5518 Solution Chemistry

5519 The radiochemistry of uranium is complicated because of the multiple oxidation states that can  
5520 exist in solution and the extensive complexation and hydrolytic reactions the ions are capable of  
5521 undergoing in solution. Four oxidation states are possible: +3, +4, +5, and +6; the latter two exist  
5522 as oxyocations:  $\text{UO}_2^{+1}$  and  $\text{UO}_2^{+2}$ , respectively. Their stabilities vary considerably, and the +4 and  
5523 +6 states are stable in solution under certain conditions; oxidation-reduction reagents are used to  
5524 form and maintain these ions in solution. Each ion has different chemical properties, and those of  
5525 the +4 and +6 states have been particularly exploited to stabilize, solubilize, separate, and collect  
5526 uranium. The multiple possibilities of oxidation state, complexation, and hydrolysis should be  
5527 carefully considered when planning any radiochemical procedures.

5528 OXIDATION-REDUCTION BEHAVIOR. The multiple oxidation states can be exploited during  
5529 separation procedures by taking advantage of their different chemical properties. Thorium can be  
5530 separated from uranium, for example, by oxidizing uranium in solution to the +6 oxidation state  
5531 with 30 percent hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and precipitating thorium as the hydroxide; in the +6  
5532 state, uranium is not precipitated.

5533 The U<sup>+3</sup> ion is an unstable form of uranium, produced in perchlorate or chloride solutions by  
5534 reduction of UO<sub>2</sub><sup>+2</sup> electrochemically or with zinc amalgam. It is a powerful reducing agent, and  
5535 is oxidized to U<sup>+4</sup> by chlorine or bromine. U<sup>+3</sup> is slowly oxidized by water with the release of  
5536 hydrogen, and oxygen from air causes rapid oxidation. Aqueous solutions are red-brown and are  
5537 stable for several days in 1 M hydrochloric acid, especially if kept cold; rapid oxidation occurs in  
5538 more concentrated acid solutions.

5539 The tetrapositive uranous ion, U<sup>+4</sup>, is produced by dissolving water-soluble salts of the ion in  
5540 solution, dissolving uranium metal with sulfuric or phosphoric acid, reduction of UO<sub>2</sub><sup>+1</sup> during its  
5541 disproportionation reaction, reduction of UO<sub>2</sub><sup>+2</sup> by Cr<sup>+2</sup> or Ti<sup>+3</sup>, or oxidation of U<sup>+3</sup>. The tetraposi-  
5542 tive ion is green in solution. The ion is stable, but slowly oxidizes by oxygen from air to the +6  
5543 state.

5544 The UO<sub>2</sub><sup>+1</sup> ion (+5 state) is extremely unstable in solution and exist only as a transient species,  
5545 disproportionating rapidly to U<sup>+4</sup> and UO<sub>2</sub><sup>+2</sup> according to the following reaction in the absence of  
5546 complicating factors (k=1.7 x 10<sup>6</sup>):



5548 Maximum stability is observed in the pH range 2–4 where the reaction is considerably slower.  
5549 Solutions of UO<sub>2</sub><sup>+1</sup> are prepared by the dissolution of UCl<sub>5</sub> or reduction of UO<sub>2</sub><sup>+2</sup> ions  
5550 electrochemically or with U<sup>+4</sup> ions, hydrogen, or zinc amalgam.

5551 The +6 oxidation state of uranium is generally agreed to be in the form of the dioxo or uranyl ion,  
5552 UO<sub>2</sub><sup>+2</sup>. As the only oxidation state stable in contact with air, it is very stable in solution and  
5553 difficult to reduce. Because of its exceptional stability, the uranyl ion plays a central role in the  
5554 radiochemistry of uranium. It is prepared in solution by the dissolution of certain water-soluble  
5555 salts: nitrate, halides, sulfate, acetate, and carboxylates; by dissolution of uranium +6  
5556 compounds; and oxidation of lower-oxidation state ions already in solution, U<sup>+4</sup> with nitric acid  
5557 for example. Its solutions are yellow in color.

5558 COMPLEXATION. Uranium ions form numerous complex ions, and the solution chemistry of  
5559 uranium is particularly sensitive to complexing agents present. Complex-ion chemistry is very  
5560 important, therefore, to the radiochemical separation and determination of uranium.  
5561 Complexation, for example, provides a method to prevent the removal of uranium ions or its  
5562 contaminants from solution and can influence the stability of ions in solution.

5563 Among the oxidation states exhibited in solution, the tendency for formation of anionic  
5564 complexes is:



5566 while the order of stability of the anionic complexes is represented by:

5567 fluoride > nitrate > chloride > bromide > iodide > perchlorate > carbonate > oxalate > sulfate.

5568 Numerous organic complexes form, including citrate, tartrate, and EDTA, especially with  $UO_2^{+2}$ .

5569 There is evidence for only a few complexes of  $U^{+3}$ , cupferron and chloride for example. In  
5570 contrast, tetrapositive uranium,  $U^{+4}$ , forms complexes with a wide variety of anions, and many  
5571 are stable: halides—including fluoride (up to eight ligands,  $UF_8^{-4}$ )—chloride, and bromide;  
5572 thiocyanate; and oxygen-donors, nitrate, sulfates, phosphates, carbonate, perchlorate, and  
5573 numerous carboxylates: acetate, oxalate, tartrate, citrate, and lactate. The low charge on  $UO_2^{+1}$   
5574 precludes the formation of very stable complexes. Fluoride (from hydrogen fluoride) is notable,  
5575 however, in its ability to displace oxygen from the ion, forming  $UF_6^{-1}$ —which inhibits  
5576 disproportionation—and precipitating the complex ion from aqueous solution. The uranyl ion,  
5577  $UO_2^{+2}$ , readily forms stable complexes with a large variety of inorganic and carboxylate anions  
5578 very similar to those that complex with  $U^{+4}$ . In addition, numerous organic ligands besides  
5579 carboxylates are known that contain both oxygen and nitrogen as donor atoms. Complex-ion  
5580 formation must be considered, therefore, during precipitation procedures. Precipitation of  
5581 uranium ions is inhibited, for example, in solutions containing carbonate, tartrate, malate, citrate,  
5582 hydroxylamine, while impurities are precipitated as hydroxides, sulfides, or phosphates.  
5583 Conversely, uranium is precipitated with ammonia, while other ions are kept in solution as  
5584 complexes of EDTA.

5585 HYDROLYSIS. Some uranium ions undergo extensive hydrolysis in aqueous solution. The  
5586 reactions can lead to formation of polymeric products, which form precipitates under certain  
5587 conditions. The tendency of the various oxidation states toward hydrolysis, a specific case of  
5588 complexation, is, therefore, in the same order as that of complex-ion formation (above).

5589 Little data are available on the hydrolysis of  $U^{+3}$  ion because it is so unstable in solution.  
5590 Qualitative evidence indicates, however, that hydrolysis is about that to be expected for a +3 ion  
5591 of its size, that is, as a much weaker acid than most other metals ions of this charge. The  $U^{+4}$  ion  
5592 is readily hydrolyzed in solution, but exist as the unhydrolyzed, hydrated ion in strongly acidic  
5593 solutions. Hydrolysis begins at  $pH < 1$ , starting with the  $U(OH)^{+3}$  species. An increase in pH,  
5594 several species form progressively up to  $U(OH)_5^{-1}$ . The  $U(OH)^{+3}$  species predominates at high  
5595 acidity and low uranium concentrations, and the concentration of each species increases rapidly  
5596 with the temperature of the solution. In less acidic solutions and as the concentration of uranium  
5597 increases, a polymeric species forms, probably  $U_6(OH)_{15}^{+9}$ . Hydrolytic complexes of high  
5598 molecular weight probably form subsequently, culminating in precipitation. Hydrolysis of the  
5599  $UO_2^{+1}$  ion has been estimated to be very low, consistent with the properties of a large, positive  
5600 ion with a single charge. Hydrolysis of  $UO_2^{+2}$  begins at about pH 3 and is fairly complicated. In  
5601 very dilute solutions, the monomeric species,  $UO_2(OH)^{+1}$ , forms initially; but the dimerized  
5602 species,  $(UO_2)_2(OH)_2^{+2}$ , rapidly becomes the dominant form in solution, existing in a wide range  
5603 of uranium concentration and pH. As the pH increases, more complex polynuclear species  
5604 become prominent. The presence of complexing agents, such as chloride, nitrate, and sulfate ions  
5605 suppress hydrolysis to varying degrees.

5606 Dissolution of Samples

5607 Metallic uranium dissolves in nitric acid to form uranyl nitrate. Large amounts dissolve  
5608 moderately rapidly, but fine turnings or powder may react violently with nitric acid vapors or  
5609 nitrogen dioxide in the vapor. The presence of oxygen in the dissolution system tends to reduce  
5610 the oxides. The rate of dissolution of large amounts of uranium may be increased by the addition  
5611 of small amounts of sulfuric, phosphoric, or perchloric acids to the nitric acid solution. Other  
5612 common mineral acids such as sulfuric, phosphoric, perchloric, hydrochloric, and hydrobromic  
5613 acid are also used to dissolve uranium metal. Simple organic acids in hydrochloric acid dissolve  
5614 the metal, and other solvent systems are used: sodium hydroxide and hydrogen peroxide,  
5615 bromine in ethyl acetate, and hydrogen chloride in ethyl acetate or acetone. Uranium compounds  
5616 are dissolved in numerous solvents and solvent combinations such as water, mineral acids,  
5617 organic solvents such as acetone, alcohols, and diethyl ether. Dissolution of uranium from  
5618 minerals and ores is accomplished by decomposition of the sample or leaching the uranium.  
5619 Grinding and roasting the sample facilitates recovery. Decomposition of the sample can be  
5620 accomplished with mineral acids or by fusion or a combination of the two processes.  
5621 Hydrofluoric acid aids the process. The sample can be fused with sodium carbonate, sodium  
5622 hydroxide, sodium peroxide, sodium bisulfate, ammonium sulfate, lithium metaborate, and  
5623 magnesium oxide. The fused sample is dissolved in water or acid. Acid and alkaline mixtures are  
5624 used to leach uranium from minerals and ores. The procedures employ common mineral acids or

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5625 alkaline carbonates, hydroxides, and peroxides. Liquid biological samples may also be extracted  
5626 to remove uranium, or the solid sample can be ashed by a wet or dry process and dissolved in  
5627 acid solution. Wet ashing is carries out with nitric acid and completed with perchloric acid, but  
5628 extreme caution should be used when using perchloric acid in the presence of organic material.

## 5629 Separation Methods

5630 PRECIPITATION AND COPRECIPITATION. There are a large number of reagents that will precipitate  
5631 uranium over a wide pH range. The number of reagents available coupled with the two possible  
5632 oxidation states of uranium in solution and the complexing properties of the ions provide many  
5633 opportunities to separate uranium from other cations and the two oxidation states from each  
5634 other. Precipitation can be inhibited, for example, by the presence of complexing agents that  
5635 form soluble complexes. Complexes that form weak complexes with uranium and strong  
5636 complexes with other cations allow the separation of uranium by its precipitation while the  
5637 complexed cations remain in solution. EDTA has been used in this manner to separate uranium  
5638 form many of the transition metals and alkaline earths. In contrast, uranium forms a very strong  
5639 soluble complex with carbonate, and this property has been used to keep uranium in solution  
5640 while ammonium hydroxide precipitates iron, titanium, zirconium, and aluminum. In a similar  
5641 manner, uranium is separated from other cations as they are precipitated as sulfides or  
5642 phosphates. Common precipitating reagents and used for separation include: ammonium  
5643 hydroxide, precipitates uranium quantitatively at  $\text{pH} \geq 4$ ; carbonate, which will form soluble  
5644 anionic complexes with uranium (VI) at pH 5 to 11 while many other metals form insoluble  
5645 hydroxides; peroxide; oxalic acid, completely precipitate uranium (IV) while uranium (VI) forms  
5646 a soluble complex; iodide; iodate; phosphate for uranium (VI) over a wide pH range; sulfate;  
5647 cupferron, precipitates uranium (IV) from an acidic solution but uranium (VI) from a neutral  
5648 solution; and 8-hydroxyquinoline, which forms a quantitatively precipitate with uranium(VI)  
5649 only.

5650 Coprecipitation of uranium is accomplished with several carriers. In the absence of carbonate, it  
5651 is quantitatively coprecipitated with ferric hydroxide at pH from 5 to 8. Aluminum and calcium  
5652 hydroxide are also employed to coprecipitate uranium. Uranium (VI), however, is only partially  
5653 carried by metal hydroxides in the presence of carbonate, and the amount carried decreases as the  
5654 concentration of carbonate increases. Small amounts of uranium (VI) coprecipitate with ceric  
5655 and thorium fluoride, calcium, zirconium, and aluminum phosphate, barium carbonate, thorium  
5656 hexametaphosphate, magnesium oxide, and thorium peroxide. Uranium (IV) is carried on ceric  
5657 sulfate, the phosphates of zirconium, bismuth, and thorium, lanthanum and neodymium fluoride,  
5658 ceric and zirconium iodates, barium sulfate, zirconium phosphate, and bismuth arsenate.

5659 SOLVENT EXTRACTION. Liquid-liquid extraction is the most common method for the separation  
5660 of uranium in radioanalytical procedures. Extraction provides a high-recovery, one-batch process  
5661 that is more reproducible than other methods. With the development of extraction chromatog-  
5662 raphy, solvent extraction has become a very efficient process for uranium separation. Many and  
5663 varied procedures are used to extract uranium from aqueous solutions, but the conditions can be  
5664 summarized as: (1) composition of the aqueous phase (form of uranium, type of acid present, and  
5665 presence of common cations and anions and of foreign anions); (2) nature of organic phase (type  
5666 and concentration of solvent and diluent); (3) temperature; and (4) time of equilibrium.  
5667 Extraction processes can be conveniently divided into three systems: those based on (1) oxygen  
5668 bonding, (2) chelate formation, and (3) extraction of anionic complexes.

5669 Oxygen-bonding systems are more specific than those based on chelate formation. The employ  
5670 organic acids, ethers, ketones, esters, alcohols, organophosphates (phosphoesters), and  
5671 nitroalkanes. Ethers are effective for the extraction of uranyl nitrate from nitric acid solutions.  
5672 Cyclic ethers are especially effective, and salting agents such as calcium nitrate increase the  
5673 effectiveness. Methyl isobutyl ketone (MIBK or hexone) also effectively extracts uranium as the  
5674 nitrate complex. It has been used extensively by industry in the Redox process for extracting  
5675 uranium and plutonium from nuclear fuels. Aluminum hydroxy nitrate  $[AlOH(NO_3)_2]$  is an  
5676 excellent salting agent for the process and the extraction efficiency is increased by the presence  
5677 of the tetrapropylammonium cation  $[(C_3H_7)_4N^{+}]$ . Another common system, used extensively in  
5678 the laboratory and in industrial process to extract uranium and plutonium from fission products,  
5679 known as the PUREX process (plutonium uranium reduction extraction), is used in most fuel  
5680 reprocessing plants to separate the radionuclides. It employs TBP, tri-*n*-butyl phosphate  
5681  $[(C_4H_9)_3PO]$ , in a hydrocarbon solvent, commonly kerosene, as the extractant. The uranium fuel  
5682 is dissolved in nitric acid, and uranium and plutonium are extracted into a 30 percent TBP  
5683 solution, forming a neutral complex,  $UO_2(TBP)_2$ . The organic phase is scrubbed with nitric acid  
5684 solution to remove impurities, plutonium is removed by back-extracting it as Pu(III) with a nitric  
5685 acid solution containing a reducing agent, and uranium is removed with dilute nitric acid. A  
5686 complexing agent can also be used as a stripping agent. Trioctylphosphine oxide is 100,000 times  
5687 more efficient in extracting uranium (VI). In both cases, nitric acid is used both to form the  
5688 uranium extracting species, uranyl nitrate, and as the salting agent. Salting with aluminum nitrate  
5689 produces a higher extraction efficiency but less specificity for uranium. Specificity depends the  
5690 salt used and its concentration and the diluent concentration.

5691 Uranium is also extracted with select chelate forming agents. One of the most common systems  
5692 used for uranium is cupferron in diethyl ether or chloroform. Uranium (VI) is not extracted from  
5693 acidic media, so impurities soluble in the mixture under acidic conditions can be extracted first.

5694 Uranium (VI) can be reduced to uranium (IV) for subsequent extraction. Other chelating agents  
5695 used to extract uranium include 8-hydroxyquinoline or acetylacetone in hexone or chloroform.

5696 Amines with molecular weights in the 250 to 500 range are used to extract anionic complexes of  
5697 uranium (VI) from acidic solutions. The amine forms a salt in the acidic medium consisting of a  
5698 ammonium cation and complex anion,  $(C_{10}H_{21})_3NH^{+1} UO_2(NO_3)^{-1}$ , for example. Selectivity of the  
5699 amines for uranium (VI) is in the order: tertiary > secondary > primary. An anionic extracting  
5700 system use extensively in laboratories and industry consists of triisooctyl amine (TIOA) in  
5701 kerosene. Uranium is stripped with sodium sulfate or sodium carbonate solution. A number of  
5702 mineral and organic acids have been used with the system: hydrochloric, sulfuric, nitric,  
5703 phosphoric, hydrofluoric, acetic oxalic, formic, and maleic acid. Stripping is accomplished with  
5704 dilute acid solutions.

5705 Extraction chromatography is a simple and relatively quick method for the separation of uranium  
5706 on a highly selective, efficient column system. One separation column consist of a triamyl-  
5707 phosphate  $[(C_5H_{11}O)_3PO]$  and diamylamylphosphonate (DAAP)  $[C_5H_{11}O)_2(C_5H_{11})PO]$  mixture in  
5708 an apolar polymeric matrix. In nitric acid, uranyl nitrate forms a complex with DAAP that is  
5709 soluble in triamylphosphate. Uranium can be separated in this system from many other metal  
5710 ions, including thorium and the transuranium ions plutonium, americium, and neptunium. It is  
5711 eluted from the column with the addition of oxalate to the eluent. Another extraction chromatog-  
5712 raphy column uses octylphenyl-N,N-diisobutyl carbamoylphosphine oxide (CMPO) dissolved in  
5713 TBP and fixed on the resin matrix for isolation of uranium in nitric acid. Elution occurs with the  
5714 addition of oxalic acid to the eluent.

5715 ION-EXCHANGE CHROMATOGRAPHY. Both cation- and anion-exchange chromatography have  
5716 been used to separate uranium from other metal ions. Both stable forms of uranium, uranium (IV  
5717 and VI) are absorbed on cation-exchange resins. Uranium (IV) is more strongly absorbed, and  
5718 separation of uranium (VI) ( $UO_2^{+2}$ ) is limited. On some cation-exchange columns, the ion also  
5719 tends to tail into other ion fractions during elution. Absorption increases with temperature,  
5720 however, and increasing the pH also increases absorption up to the beginning of formation of  
5721 hydrolytic precipitates at pH 3.8. In strong acid solutions, uranium (VI) is weakly absorbed  
5722 compared to uranium (III and IV) cations. Use of complexing agents increases specificity either  
5723 by elution of uranium (VI) with common complexes-forming anions such as chloride, fluoride,  
5724 nitrate, carbonate, and sulfate or by forming EDTA, oxalate, acetate, or sulfate complexes with  
5725 cations in the analyte, producing a more pronounced difference in absorption of the ions on the  
5726 exchange resin. A general procedure for separating uranium (VI) from other metals using the first  
5727 method is to absorb uranium (VI) at pH of 1.5 to 2 and elute the metal with acetate solution.

5728 Anion-exchange chromatography of uranium takes advantage of the stable anionic complexes  
5729 formed by the various oxidation states of uranium, especially uranium (VI), with many common  
5730 anions. Uranium (VI) forms both anionic or neutral complexes with acetate, chloride, fluoride,  
5731 carbonate, nitrate, sulfate, and phosphate. Strong anion-exchange resins are more selective and  
5732 have a greater capacity than weak exchangers whose use is more limited. Factors that affect the  
5733 separations include uranium oxidation state and concentration; type of anion and concentration;  
5734 presence and concentration of other metallic ions and foreign ions; temperature, resin, size,  
5735 porosity, and cross-linking. The various oxidation states of uranium and other metal ions,  
5736 particularly the actinides, and the effect of pH on formation of complexes and net charge of the  
5737 column provide two controllable variable to control the separation process.

5738 A number of chromatographic systems are available for uranium separation on anion-exchange  
5739 resins. In hydrochloric acid uranium is often absorbed and other cations are not. Uranium (VI)  
5740 can be absorbed from concentrated hydrochloric acid while alkali metals, alkaline earths, rare  
5741 earths, aluminum, yttrium, actinium, and thorium are washed off the column. In contrast,  
5742 uranium, molybdenum, bismuth, tin, technetium, polonium, plutonium and many transition  
5743 metals are absorbed on the column, and uranium is eluted exclusively with dilute hydrochloric  
5744 acid. Various oxidation states provide another method of separation. Uranium (IV) is separated  
5745 from praseodymium (IV), and thorium (IV) with 8 M hydrochloric acid. Thorium, plutonium,  
5746 zirconium, neptunium, and uranium can be separated individually by absorbing all the ions  
5747 except thorium from concentrated hydrochloric acid Plutonium (III) elutes with concentrated  
5748 acid, zirconium at 7.5 M, neptunium (IV) with 6 M hydrochloric acid and 5 percent  
5749 hydroxylamine hydrochloride, and uranium at 0.1 M acid. Uranium (IV) can be separated from  
5750 uranium (VI) because both strongly absorb from concentrated hydrochloric acid, but they  
5751 separate at 6 M acid because uranium (IV) is not absorbed at that concentration. Uranium (VI)  
5752 absorbs strongly on an anion-exchange resin in dilute hydrofluoric acid, and the absorption  
5753 decreases with increasing acid concentration. Nitric acid provides an excellent method to purify  
5754 uranium, because uranium is more strongly absorbed from a nitric acid/nitrate solution. More  
5755 selectivity is achieved when acid concentration is low and nitrate concentrations high.  
5756 Absorbance is greatest when aluminum nitrate is use as the source of nitrate. Ethyl alcohol  
5757 increases absorbance significantly.

5758 ELECTRODEPOSITION. Electrochemical procedures have been used to separate metal ions from  
5759 uranium in solution by depositing them on a mercury cathode from a sulfuric acid solution, using  
5760 5 amps for one hour. Uranium is deposited at a cathode from acetate, carbonate, oxalate, formate,  
5761 phosphate, fluoride, and chloride solutions to produce a thin, uniform film for alpha and fission  
5762 counting. This is the primary use of electrodeposition of uranium in analytical work. In another  
5763 procedure, uranium (VI) is electroplated on a platinum electrode from the basic solution adjacent

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5764 to the cathode that exist in a slightly acidic bulk solution. The conditions of the process should be  
5765 carefully controlled to obtain high yields and adherent coatings on the electrode.

5766 VOLATILIZATION. Several halides of uranium and the uranyl ion are volatile and have the  
5767 potential for separation by sublimation or fractional distillation. Practically, however, their  
5768 volatility is not used to separate uranium in analytical procedures because of technical problems  
5769 or the high temperatures that are required for some procedures, but volatilization has been used  
5770 in industrial processes. Uranium hexafluoride and uranyl hexafluoride are volatile, and the  
5771 property is used to separate  $^{235}\text{U}$  from  $^{238}\text{U}$  in natural uranium isotope mixtures. Uranium tetra-  
5772 chloride and hexachloride are also volatile, and uranium has been isolated from phosphate rock  
5773 by heating with a mixture of chlorine and carbon monoxide at 800 °C and collecting the  
5774 tetrachloride.

### 5775 Methods of Analysis

5776 Macroquantities of uranium, essentially  $^{238}\text{U}$ , are determined by fluorimetry. During the  
5777 separation and purification process, the sample is eventually fused at 625 °C in a flux mixture  
5778 containing potassium carbonate, sodium carbonate, and sodium fluoride. The residue is exposed  
5779 to light and its fluorescence is measured. Total uranium or individual radionuclides of uranium,  
5780  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ , can be determined from their alpha particle emissions. Uranium radionuc-  
5781 lides are collected by evaporating the sample to dryness on a stainless steel planchet, by micro-  
5782 precipitation with a carrier, such as lanthanum or cerium fluoride, or electrodeposition on a  
5783 platinum disc. Total alpha activity is determined with a gas-flow proportional counter or an alpha  
5784 liquid scintillation system. Individual radionuclides are measured by alpha spectrometry. Alpha  
5785 emissions from  $^{232}\text{U}$  are used as a tracer to determine chemical recovery.

5786 Compiled from: Allard et al., 1984; Ahrlund, 1986; Baes and Mesmer, 1976; Bard, 1985;  
5787 Booman and Rein, 1962; Choppin et al., 1995; Considine and Considine, 1983; Cotton and  
5788 Wilkinson, 1988; CRC, 1998-99; DOE, 1990, 1995, and 1997; EPA, 1973; Ehmann and  
5789 Vance, 1991; Fritz and Weigel, 1995; Greenwood and Earnshaw, 1984; Grindler, 1962;  
5790 Hampel, 1968; Hassinsky and Adloff, 1965; Katz et al., 1986; Katzin, 1986; SCA, 2001;  
5791 Weigel, 1986.

### 5792 14.10.9.12 Zirconium

5793 Zirconium, atomic number 40, is a member of the second-row transition elements. It exhibits  
5794 oxidation states of +2, +3, and +4, and the +4 state is the most common in both the solid state  
5795 and in solution. It is immediately above hafnium in the periodic table, and both elements have

5796 very similar chemical properties, more so than any other two elements in the periodic table. It is  
5797 very difficult, but not impossible, to prepare a sample of zirconium without the presence of  
5798 hafnium.

5799 Isotopes

5800 There are twenty-nine isotopes of zirconium, including five metastable states, with mass numbers  
5801 from 81 through 104. Five are naturally occurring,  $^{90}\text{Zr}$ ,  $^{91}\text{Zr}$ ,  $^{92}\text{Zr}$ ,  $^{94}\text{Zr}$ , and  $^{96}\text{Zr}$ , although the  
5802 least abundant,  $^{96}\text{Zr}$ , is radioactive with an exceptionally long half-life of  $3.56 \times 10^{17}$  y. The  
5803 remaining isotopes have a half-life of milliseconds to days. The lower mass number isotopes  
5804 decay primarily by electron capture and the upper mass number isotopes are beta emitters.  $^{95}\text{Zr}$   
5805 ( $t_{1/2}=64.0$  d) and  $^{97}\text{Zr}$  ( $t_{1/2}=16.9$  h) are fission products and are beta emitters.  $^{93}\text{Zr}$  ( $t_{1/2}=1.53 \times 10^6$  y)  
5806 is a rare fission product, and  $^{98}\text{Zr}$ , and  $^{99}\text{Zr}$  are short-lived products with half-lives of 30.7 s and  
5807 2.1 s, respectively. All are beta emitters.

5808 Occurrence and Uses

5809 Zirconium is one of the most abundant and widely distributed metals found in the earth's crust. It  
5810 is so reactive that it is found only in the combined state, principally in two minerals, zircon,  
5811 zircon orthosilicate ( $\text{ZrSiO}_4$ ), and baddeleyite, mostly zirconium dioxide ( $\text{ZrO}_2$ ). Zirkite is a  
5812 commercial ore that consists of both minerals. Hafnium is a minor constituent of all zirconium  
5813 minerals.

5814 In the production of zirconium metal, zirconium sands, primarily zirconium dioxide, is passed  
5815 through an electrostatic separator to remove titanium minerals, a magnetic separator to remove  
5816 iron, ilmenite, and garnet, and a gravity separator to remove the less dense silica. The recovered  
5817 zircon is heated with carbon in an arc furnace to form zirconium cyanonitride, an interstitial  
5818 solution of carbon, nitrogen, and oxygen (mostly carbon) in the metal. Silicon evaporates as  
5819 silicon monoxide ( $\text{SiO}$ ), becoming silicon dioxide ( $\text{SiO}_2$ ) at the mouth of the furnace. The hot  
5820 zirconium cyanonitride is treated with chlorine forming volatile zirconium tetrachloride ( $\text{ZrCl}_4$ ),  
5821 which is purified by sublimation to remove, among other impurities, contaminating oxides. The  
5822 chloride is reduced in the Kroll process, in turn, with liquid magnesium under conditions that  
5823 produce a metal sponge. The byproduct, magnesium chloride ( $\text{MgCl}_2$ ), is then removed by  
5824 melting the chloride, draining it off, and removing its residues by vacuum distillation. The  
5825 zirconium sponge is crushed, melted into bars, arc-melted in an inert atmosphere, and formed  
5826 into ingots. For additional purification, the van Arkel-de Boer process removes all nitrogen and  
5827 oxygen. Crude zirconium is heated to  $200^\circ\text{C}$  in an evacuated container containing a small  
5828 amount of iodine to form volatile zirconium tetraiodide ( $\text{ZrI}_4$ ). A tungsten filament is electrically

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5829 heated to 1,300 °C, decomposing the iodide and depositing zirconium on the filament. The  
5830 commercial grade of zirconium still contains up to three percent hafnium. To be used in nuclear  
5831 reactors, however, hafnium should be removed. Separation is usually accomplished by solvent  
5832 extraction of zirconium from an aqueous solution of zirconium tetrachloride as a complex ion  
5833 (phosphine oxide, for example), by ion-exchange, fractional crystallization of complex fluoride  
5834 salts, distillation of complexes of zirconium tetrachloride with phosphorus pentachloride or  
5835 phosphorus oxychloride, or differential reduction of the mixed tetrachlorides (zirconium  
5836 tetrachloride is more easily reduced to the nonvolatile trichloride than hafnium tetrachloride.

5837  $^{95}\text{Zr}$  and  $^{97}\text{Zr}$  are fission products and are also produced by bombardment of naturally occurring  
5838  $^{94}\text{Zr}$  and  $^{96}\text{Zr}$ , respectively, with thermal neutrons. Stable  $^{90}\text{Zr}$  is a product of the  $^{90}\text{Sr}$  decay chain:



5840 Zirconium metal and its alloys are highly corrosion resistant and withstands streams of heated  
5841 water under high pressure. These properties, along with their low cross section for thermal  
5842 neutrons, make them an important material for cladding uranium fuel elements and as core armor  
5843 material in nuclear reactors. It is also used for making corrosive resistant chemical equipment  
5844 and surgical instruments and making superconducting magnets. Zirconium compounds are also  
5845 used in the ceramics industry as refractories, glazes, and enamels, in cores for foundry molds,  
5846 abrasive grits, and components of electrical ceramics. Crystals of zircon are cut and polished to  
5847 use in jewelry as simulated diamonds. They are also used in pyrotechnics, lamp filaments, in arc  
5848 lamps, cross-linking agents for polymers, components of catalysts, as bonding agents between  
5849 metal and ceramics and between ceramics and ceramics, as tanning agents, ion exchangers, and  
5850 in pharmaceutical agents as deodorants and antidotes for poison ivy.  $^{95}\text{Zr}$  is used to follow  
5851 homogenization of oil products.

### 5852 Solubility of Compounds

5853 The solution properties of zirconium in water are very complex, mainly because of the formation  
5854 of colloids and the extensive hydrolysis and polymerization of the zirconium ion. hydrolysis and  
5855 polymerization are strongly dependent on the pH of the solution, concentration of the ion, and  
5856 temperature. The nitrate, chloride, bromide, iodide, perchlorate, and sulfate of zirconium are  
5857 soluble in acid solution, however.

5858 Review of Properties

5859 Pure zirconium is a grey-white (silvery) lustrous metal with a density of 6.49 g/cm<sup>3</sup>. It exist in  
5860 two allotropic forms, alpha and beta, with a transition temperature of 870 °C. The alpha form is  
5861 stabilized by the common impurity oxygen. The amorphous powder is blue-black. Trace amounts  
5862 of common impurities (≤1 percent), such as oxygen, nitrogen, and carbon, make the metal brittle  
5863 and difficult to fabricate. The metal is not considered to be a good conductor of heat and  
5864 electricity, but compared to other metals it is soft, malleable, and ductile. Zirconium forms alloys  
5865 with most metals except, mercury, the alkali metals, and the alkaline earths. It can absorb up to  
5866 ten percent oxygen and nitrogen. Zirconium is a superconductor at temperatures near absolute  
5867 zero, but its superconducting properties improve when the metal is alloyed with niobium and  
5868 zinc.

5869 Finely divided, dry zirconium (powder and chips) is pyrophoric and extremely hazardous. It is  
5870 hard to handle and store and should be moistened for safe use. Note, however, that both wetted  
5871 sponge and wet and dry stored scrap have been reported to spontaneously explode. Caution  
5872 should also be observed with waste chips produced from machining and cleaning (new)  
5873 zirconium surfaces. Both can be pyrophoric. In contrast, zirconium in the bulk form is extremely  
5874 resistant to corrosion at room temperature and remains bright and shiny in air. Resistance is  
5875 rendered by the formation of a dense, adherent, self-sealing oxide coating. The metal in this form  
5876 is resistant to acids, alkalis, and seawater. Without the coating, zirconium dissolves in warm  
5877 hydrochloric and sulfuric acids slowly; dissolution is more rapid in the presence of fluoride ions.  
5878 The metal is also resistant to high-pressure water streams and high-temperature steam. It also has  
5879 a low cross-section to thermal neutrons and is resistant to damage from neutron radiation. These  
5880 properties give pure zirconium (without hafnium) very useful as a fabrication material for nuclear  
5881 reactors. Zirconium metal alone, however, is not sufficiently resistant to hot water and steam to  
5882 meet the needs for use in a nuclear reactor. Alloyed with small percentages of tin, iron, nickel, or  
5883 chromium (Zircalloy), however, the metal meets the standards.

5884 The coated metal is becomes reactive when heated at high temperature (≥ 500 °C) with  
5885 nonmetals, including hydrogen, oxygen, nitrogen, carbon, and the halogens, and forms solid  
5886 solutions or compounds with many metals. It reacts slowly with hot concentrated sulfuric and  
5887 hydrochloric acids, boiling phosphoric acid, and aqua regia. It is also attacked by fused potassium  
5888 nitrate and potassium hydroxide, but is nonreactive with aqueous alkali solutions. It is not  
5889 reactive with nitric acid. Hydrofluoric acid is the only reagent that reacts vigorously with  
5890 zirconium.

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5891 Zirconium and its compounds are considered to have a low order of toxicity. Most handling and  
5892 testing indicate no level of toxicity, but some individual seem to be allergic to zirconium  
5893 compounds. Inhalation of zirconium compound sprays and metallic zirconium dust have  
5894 produced inflammatory affects.

5895 Very small quantities of  $^{95}\text{Zr}$  have been released to the environment from fuel reprocessing  
5896 facilities, atmospheric testing, and the Chernobyl accident. With a half-life of 64 days, the  
5897 contamination of the environment is not significant. Zirconium lost from a waste repository  
5898 would be expected to move very slowly because of radiocolloidal attraction to surrounding soil  
5899 particles. Hydrolysis and polymerization renders most zirconium insoluble in natural water, but  
5900 absorption to suspended particles is expected to provide some mobility in an aqueous  
5901 environment.

### 5902 Solution Chemistry

5903 The only important oxidation state of zirconium ions in aqueous solution is +4, making it a  
5904 essentially a monovalent element. The solution chemistry of zirconium is quite complex,  
5905 nevertheless, because of the easy formation of colloids and extensive hydrolysis and  
5906 polymerization reactions that are strongly dependent on pH and ion concentration.

5907 COMPLEXATION. Zirconium ions forms complexes with numerous substances: fluoride,  
5908 carbonate, borate, oxalate, and other dicarboxylic acids, among others. As a large, highly  
5909 charged, spherical ion, it exhibits high coordination numbers. One of the important chemical  
5910 properties of zirconium ions in solution is their formation of a very stable hexafluorozirconate  
5911 complex,  $\text{ZrF}_6^{-2}$ . For that reason, hydrofluoric acid (HF) is an excellent solvent for the metal and  
5912 insoluble zirconium compounds. Unfortunately, the fluoro complex interferes with most  
5913 separation and determination steps, and zirconium should be expelled by fuming with sulfuric or  
5914 perchloric acid before proceeding. The addition of several milliliters of concentrated HF to a cool  
5915 solution of zirconium carrier and sample will produce initial equilibration; essentially all the  
5916 zirconium is present in the +4 oxidation state as a fluoride complex. Note that addition of HF to  
5917 solutions above the azeotropic boiling point of the acid (120 °C) serves no useful purpose and  
5918 simply evaporates the HF.

5919 Tartrate and citrate ions form stable complexes even in alkaline solutions, and zirconium  
5920 hydroxide will not precipitate in their presence (see hydrolysis below). Oxalate forms a complex  
5921 that is less stable. The ion,  $[\text{Zr}(\text{C}_2\text{O}_4)_3]^{-2}$ , is only stable in acid solution. On addition of base, the  
5922 complex is destroyed, and zirconium hydroxide precipitates. Sulfuric acid complexes in strongly  
5923 acidic solutions, forming  $\text{Zr}(\text{SO}_4)_4^{-2}$ . In concentrated HCl solutions,  $\text{ZrCl}_6^{-2}$  is present.

5924 Zirconium ions form chelate complexes with many organic compounds, usually through oxygen  
5925 atoms in the compounds. Typical examples are: acetylacetone (acac), EDTA, thenoyltrifluoro-  
5926 acetone (TTA), salicylic acid, mandelic acid, cupferron, and 8-hydroxyquinoline.

5927 HYDROLYSIS. Although  $Zr^{+4}$  has a large radius and any +4 cation is extensively hydrolyzed,  $Zr^{+4}$   
5928 appears to exist at low ion concentrations (approximately  $10^{-4}$  M) and high pH (1-2 M). As the  
5929  $Zr^{+4}$  concentration increases and the concentration of  $H^{+1}$  decreases, however, hydrolysis and  
5930 polymerization occurs, and one or more polymeric species is dominate in solution. Amorphous  
5931 hydrous oxides are precipitated near pH 2; they are soluble in base. Because of hydrolysis,  
5932 soluble salts (nitrate, sulfate, perchlorate, acetate, and halides) form acidic solutions when they  
5933 dissolve. The reaction seems to be essentially a direct conversion to the tetranuclear  
5934  $Zr_4(OH)_8(H_2O)_{16}^{+2}$  ion; there is no convincing evidence for the existence of  $ZrO^{+2}$ , thought at one  
5935 time to be present in equilibrium with numerous other hydrolysis products. It should be noted,  
5936 however, that freshly prepared solutions of zirconium salts might react differently from a solution  
5937 left standing for several days. Whatever the actual species in solution at any given time, the  
5938 behavior of zirconium (IV) depends on the pH of the solution, temperature, anion present, and  
5939 age of solution. In addition, zirconium compounds formed by precipitation from solution usually  
5940 do not have a constant composition because of their ease of hydrolysis. Even under exacting  
5941 conditions, it is difficult to obtain zirconium compounds of known, theoretical composition, and  
5942 on aging, hydrolysis products becomes more polymeric and polydisperse.

5943 In acidic solutions, trace amounts of zirconium are strongly coprecipitated with most precipitates  
5944 in the absence of complexing ions, especially  $F^{-1}$  and  $C_2O_4^{-2}$  that form soluble complex ions.

5945 In alkaline solutions, produced by the addition of hydroxide ions or ammonia, a white gelatinous  
5946 precipitate of zirconium hydroxide forms. Since the hydroxide is not amphoteric, it does not  
5947 dissolve in excess base. The precipitate is not a true hydroxide but a hydrated oxide,  $ZrO_2 \cdot nH_2O$   
5948 where  $n$  represents the variable nature of the water content. Freshly prepared zirconium  
5949 hydroxide is soluble in acid; but as it dries, its solubility decreases. Precipitation is inhibited by  
5950 tartrate or citrate ions because  $Zr^{+4}$  forms complexes with these organic anions even in alkaline  
5951 solutions (see "Complexation," above).

5952 In preparing zirconium solutions, it is wise to acidify the solution with the corresponding acid to  
5953 reduce hydrolysis and avoid precipitation of basic salts. During solubilization and radiochemical  
5954 equilibrium with a carrier, the tendency of zirconium ions to hydrolyze and polymerize even at  
5955 low pH should be kept in mind. Often, the formation of a strong complex with fluoride or TTA is  
5956 necessary.

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5957 RADIOCOLLOIDS. Radiocolloids of zirconium are adsorbed on practically any foreign matter (e.g.,  
5958 dirt, glass, etc.). Their formation can cause problems with dissolution, achieving radiochemical  
5959 equilibrium, and analysis. Generally, it is necessary to form a strong complex with fluoride (see  
5960 caution above) or TTA.

### Dissolution of Samples

5962 Metallic zirconium is dissolved in hydrofluoric acid, hot aqua regia, or hot concentrated sulfuric  
5963 acid. Hydrofluoric acid should be removed by fuming with sulfuric acid or perchloric acid  
5964 (caution), because fluoride interferes with most separation and analytical procedures. Zirconium  
5965 ores, rocks, and minerals are fused at high temperatures with sodium carbonate, potassium  
5966 thiosulfate, sodium peroxide, sodium tetraborate, or potassium hydrogen fluoride (remove  
5967 fluoride). The residue is dissolved in dilute acid or water and might require filtration to collect a  
5968 residue of zirconia (impure  $ZrO_2$ ), which is dissolved in acid. As a minor constituent of natural  
5969 sample or as a result of formation by nuclear reactions, zirconium typically dissolves during  
5970 dissolution of the major constituents. The tendency to polymerize under low concentrations of  
5971 acid and the formation of insoluble zirconium phosphates should be considered in any  
5972 dissolution process. The tendency of zirconium to polymerize and form radiocolloids makes it  
5973 important to insure equilibrium with any carrier added. Generally, formation of strong complexes  
5974 with fluoride or TTA is necessary.

### Separation Methods

5976 PRECIPITATION AND COPRECIPITATION. One of the most insoluble precipitating agents is  
5977 ammonium hydrogen phosphate ( $(NH_4)_2HPO_4$ ) in 20 percent sulfuric acid. It has the advantage  
5978 that it can be dissolved by hydrofluoric acid, forming hexafluorozirconate. This complex ion also  
5979 forms insoluble barium hexafluorozirconate ( $BaZrF_6$ ), a precipitating agent that allows the  
5980 precipitation of zirconium in the presence of niobium that is soluble as the heptafluoronioate  
5981 ( $NbF_7^{-2}$ ). Other precipitating agents include the iodate (from 8 M nitric acid), cupferrate, the  
5982 hydroxide, peroxide, selenate, and mandelate. Cupferron is used in sulfuric or hydrochloric acid  
5983 solutions. It is one of the few precipitating agents in which fluoride does not interfere, but iron  
5984 and titanium, among other cations, are also precipitated. The precipitate can be heated in a  
5985 furnace at 800 °C to produce zirconium dioxide for the gravimetric determination of zirconium.  
5986 The hydroxide begins to precipitate at pH 2 and is complete at pH 4, depending on the presence  
5987 of zirconium complexes. It is not recommended unless other cations are absent, because it  
5988 absorbs or coprecipitates almost all other ions. Peroxide is formed from a solution of hydrogen  
5989 peroxide in acid. Selenious acid in dilute hydrochloric acid separates zirconium from some of the  
5990 transition elements and thorium. Mandelic acid in hot dilute hydrochloric acid quantitatively and

5991 specifically precipitates zirconium (and hafnium) ions. Large amounts of titanium, tin, iron, and  
5992 other ions might be partially coprecipitated, but they can be eliminated by reprecipitation.

5993 Trace quantities of zirconium can be strongly coprecipitated by most precipitates from strong  
5994 acid solutions that do not contain complex-forming ions. Bismuth and ceric phosphate readily  
5995 carries zirconium, and in the absence of holdback carriers, it is almost quantitatively carried by  
5996 rare-earth fluorides. Ferric hydroxide and thorium iodate are also effective carriers.

5997 SOLVENT EXTRACTION. Several extractants have been used to selectively remove zirconium from  
5998 aqueous solutions; most are organophosphorus compounds. Di-*n*-butylphosphoric acid (DBPA)  
5999 (di-*n*-butylphosphate) is an extractant for zirconium and niobium. It is effective in extracting  
6000 tracer and macro quantities of zirconium from 1 M aqueous solutions of nitric, hydrochloric,  
6001 perchloric, and sulfuric acids and in separating it from many other elements. A 0.06 M solution  
6002 in di-*n*-butylether containing three percent hydrogen peroxide extracts more than 95 percent  
6003 zirconium but less than one percent niobium. Tin and indium were also extracted by this mixture.  
6004 Tri-*n*-butylphosphate (TBP) is an excellent solvent for zirconium. It is used pure or with several  
6005 nonpolar diluents, ethers, kerosene, or carbon tetrachloride. Extractability increases with acid  
6006 strength. A 0.01 M solution of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane has been use  
6007 to separate zirconium form iron, molybdenum, vanadium, thorium, and hafnium.

6008 TTA and hexone (methyl isobutyl ketone) are two nonphosphorus extractants employed for  
6009 separating zirconium. TTA is highly selective. A 0.5 M solution in xylene separates zirconium  
6010 from aluminum, iron, thorium, uranium, and rare earths in a 6 M hydrochloric acid solution. At  
6011 tracers levels, the reagent can separate <sup>95</sup>Zr from all other fission products. It is also used to  
6012 separate zirconium from hafnium. In the analysis of zirconium in zirconium-niobium-tantalum  
6013 alloys, hexone separates zirconium from an aqueous solution that is 10 M hydrochloric acid and  
6014 6 M sulfuric acid. This is one of the few methods that can be use to separate zirconium from  
6015 these metals.

6016 ION-EXCHANGE CHROMATOGRAPHY. Zirconium can be separated form many other cations by  
6017 both cation- and anion-exchange chromatography. The technique represents the best laboratory  
6018 method for separating zirconium and hafnium. Cation-exchange columns strongly absorb  
6019 zirconium ions, but macro quantities of zirconium and hafnium can be purified as aqueous  
6020 colloidal solutions of their hydrous oxides on an organic cation-exchange resin. Many cations are  
6021 retained on the column, but zirconium and hafnium, under these conditions, are not. The  
6022 recovery can be as high as 99 percent with successive passages, but titanium and iron are not  
6023 removed. Zirconium and hafnium can be separated on a sulfuric-acid column from 2 M  
6024 perchloric acid. Hafnium is eluted first with 6 M hydrochloric acid. Fluoride complexes of

6025 zirconium and hafnium can be separated from other non-complexing cations, because the  
6026 negative complex ions are not absorb and the non-complexing ions are retained. Zirconium,  
6027 hafnium, and niobium are eluted from rare earths and alkaline earths on cation-exchange  
6028 columns with citrate. The three elements can be then be separated by the selection of appropriate  
6029 citrate buffers, but the separations are not quantitative.

6030 The formation of stable zirconium complexes is the basis of anion-exchange chromatography of  
6031 the metal. Separation of zirconium and hafnium from each other and form other cations can be  
6032 achieved in hydrochloric-hydrofluoric acid mixtures. Separation of zirconium from hafnium,  
6033 niobium, protactinium, and thorium, respectively, is accomplished by selection of the proper  
6034 eluting agent. Elution of hafnium first with 9 M hydrochloric acid separates zirconium from  
6035 hafnium, for example, while elution with 0.2 M hydrochloric acid/0.01M hydrofluoric acid  
6036 recovers zirconium first. Elution with 6-7 M hydrochloric acid separates zirconium from  
6037 niobium, in another example.

#### 6038 Methods of Analysis

6039 <sup>95</sup>Zr decays with a half-life of 65.5 d, emitting a beta particle accompanied by gamma-ray  
6040 emission. After several half-lives, it is in transient equilibrium with its progeny, <sup>95</sup>Nb, which has  
6041 a half-life of 35.0 d and is also a beta and gamma emitter. The progeny of <sup>95</sup>Nb is stable <sup>95</sup>Mo.  
6042 Fresh samples of <sup>95</sup>Zr are analyzed by their gamma-ray emission. Zirconium is collected by  
6043 precipitation and filtration. The sample and filter are heated at 800 °C for one hour to decompose  
6044 the filter and convert zirconium to its oxide. Zirconium dioxide (ZrO<sub>2</sub>) is collected by filtration,  
6045 dried, and counted immediately.

6046 Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Considine and Considine,  
6047 1983; Cotton and Wilkinson, 1988; CRC, 1998-99; Ehmann and Vance, 1991; EPA, 1973;  
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