14 SEPARATION TECHNIQUES

14.1 Introduction

The methods for separating, collecting, and detecting 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).

While separation techniques and principles may be found in standard textbooks, Chapter 14 addresses the basic chemical principles that apply to the analysis of radionuclides, with an emphasis on their unique behavior. It is not a comprehensive review of all techniques. This chapter provides: (1) a review of the important chemical principles underlying radiochemical separations, (2) a survey of the important separation methods used in radiochemistry with a discussion of their advantages and disadvantages, and (3) an examination of the particular features of radioanalytical chemistry that distinguish it from ordinary analytical chemistry. Extensive examples have been provided throughout the chapter to illustrate various principles, practices, and procedures in radiochemistry. Many were selected purposely as familiar illustrations from agency procedural manuals. Others were taken from the classical and recent radiochemical literature to provide a broad, general overview of the subject.

This chapter integrates the concepts of classical chemistry with those topics unique to radionuclide analysis. The first eight sections of the chapter describe the bases for chemical separations involving oxidation-reduction, complex-ion formation, distillation/volatilization, solvent extraction, precipitation and coprecipitation, electrochemistry, and chromatography. Carriers and tracers, which are unique to radiochemistry, are described in Section 14.9 together with specific separation examples for each of the elements covered in this manual. Section 14.10 also provides an overview of the solution chemistry and appropriate separation techniques for 17 elements. An attachment at the end of the chapter describes the phenomenon of radioactive equilibrium, also unique to radioactive materials.

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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, isolation of trace quantities of a radionuclide that will not precipitate on its own with a counter-ion requires judicious selection of a carrier and careful technique to produce a coprecipitate containing the pure radionuclide, free of interfering ions.

In detection procedures, the differences in the behavior of radionuclides provide unique opportunities not available in the traditional analytical chemistry of nonradioactive elements. Radionuclides often can be detected by their unique radiation regardless of the chemical form of the element. There is also a time factor involved because of the short half-lives of some radionuclides. Traditional procedures involving long digestion or slow filtration cannot be used for short-lived radionuclides, thereby requiring that rapid separations be developed. Another distinction is the hazards associated with radioactive materials. At very high activity levels, chemical effects of the radiation, such as decomposition of solvents (through radiolysis) and heat effects (caused by interaction of decay particles with the solution), can affect the procedures. Equally important, even at lower activity levels, is the radiation dose that the radiochemist can receive unless protected by shielding, ventilation, time, or distance. Even at levels where the health concerns are minimal, special care needs to be taken to guard against laboratory and equipment contamination. Moreover, the radiochemist should be concerned about the type and quantity of the waste generated by the chemical procedures employed, because the costs and difficulties associated with the disposal of low-level and mixed radioactive waste continue to rise (see Chapter 17, *Waste Management in a Radioanalytical Laboratory*).

The past 10 years have seen significant improvements to some of the classical techniques as well as the development of new methods of radiochemical analysis. Knowledge of these analytical developments, as well as maintenance of a working familiarity with developing techniques in the radiochemistry field will further enhance the waste reduction effort.

14.2 Oxidation-Reduction Processes

14.2.1 Introduction

Oxidation and reduction (redox) processes play an important role in radioanalytical chemistry, particularly from the standpoint of the dissolution, separation, and detection of analytes, tracers, and carriers. Ion exchange, solvent extraction, and solid-phase extraction separation techniques, for example, are highly dependent upon the oxidation state of the analytes. Moreover, most radiochemical procedures involve the addition of a carrier or isotope tracer. There must be complete equilibration (isotopic exchange) between the added isotope(s) and all the analyte species present in order to achieve quantitative yields. The oxidation number of a radionuclide can affect its chemical stability in the presence of water, oxygen, and other natural substances in solution; reactivity with reagents used in the radioanalytical procedure; solubility in the presence of other ions and molecules; and behavior in the presence of carriers and tracers. The oxidation numbers of radionuclides in solution and their susceptibility to change, because of natural or induced redox processes, are critical, therefore, to the physical and chemical behavior of radionuclides during these analytical procedures. The differences in mass number of all radionuclides of an element are so small that they will exhibit the same chemical behavior during radiochemical analysis (i.e., no mass isotope effects).

14.2.2 Oxidation-Reduction Reactions

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

$$U + 3\,F_2 \rightarrow U^{+6} + 6\,F^{-1}$$

$$Pu^{+4} + Fe^{+2} \rightarrow Pu^{+3} + Fe^{+3}$$

In the first reaction, uranium loses electrons, becoming a cation (oxidized), and fluorine gains an electron (reduced), becoming an anion. In the second reaction, the reactants are already ions, but the plutonium cation (Pu^{+4}) gains an electron, becoming Pu^{+3} (reduced), and the ferrous ion (Fe^{+2}) loses an electron, becoming Fe^{+3} (oxidized).

In other redox reactions, electrons are not completely transferred from one reacting species to another; the electron density of one atom decreases while it increases at another atom. The change in electron density occurs as covalent bonds (in which electrons are shared between two atoms) are broken or made during a chemical reaction. In covalent bonds between two atoms of different elements, one atom is more electronegative than the other atom. Electronegativity is the ability of an atom to attract electrons in a covalent bond. One atom, therefore, attracts the shared pair of electrons more effectively, causing a difference in electron density about the atoms in the bond. An atom that ends up bonded to a more electronegative atom at the end of a chemical reaction loses net electron density. Conversely, an atom that ends up bonded to a less electronegative atom gains net electron density. Electrons are not transferred completely to other atoms, and ions are not formed because the electrons are still shared between the atoms in the covalent bond. Oxidation, in this case, is defined as the loss of electron density, and reduction is defined as the gain of electron density. When carbon is oxidized to carbon dioxide by oxygen:

$$C + O_2 \rightarrow CO_2$$

the electron density associated with the carbon atom decreases, and that of the oxygen atoms increases, because the electronegativity of oxygen is greater than the electronegativity of carbon. In this example, carbon is oxidized and oxygen is reduced. Another example from the chemistry of the preparation of gaseous uranium hexafluoride (UF_6) illustrates this type of redox reaction:

$$3\ UF_4 + 2\ ClF_3 \rightarrow 3\ UF_6 + Cl_2$$

Because the order of electronegativity of the atoms increases in the order U < Cl < F, the uranium atom in uranium tetrafluoride (UF_4) is oxidized further as more electronegative fluorine atoms are added to the metal and shift the electron density away from uranium. Chlorine atoms break their bonds with fluorine and gain electron density (are reduced) when they bond with each other instead of the more electronegative fluorine atoms.

In a redox reaction, at least one species is oxidized and at least one species is reduced simultaneously; one process cannot occur without the other. The oxidizing agent is defined as the substance that causes oxidation of another species by accepting electron(s) from it or increasing in electron density; it is thereby reduced itself. Reducing agents lose electron(s) or electron density and are therefore oxidized. In the reduction of Pu^{+4} to Pu^{+3} by Fe^{+2}, the reducing agent donates an electron to Pu^{+4} and is itself oxidized, while Pu^{+4}, the oxidizing agent, accepts an electron from Fe^{+2} and is reduced. Generally, the nonmetallic elements are strong oxidizing reagents, and the metals are strong reducing agents.

To keep track of electrons in oxidation-reduction reactions, it is useful to assign oxidation numbers to atoms undergoing the changes. Oxidation numbers (oxidation states) are a relative indication of the electron density associated with an atom of an element. The numbers change during redox reactions, whether they occur by actual transfer of electrons or by unequal sharing of electrons in a covalent bond. The number increases as the electron density decreases, and it decreases as the electron density increases. From the standpoint of oxidation numbers and in more general terms, oxidation is defined as an increase in oxidation number, and reduction is defined as the decrease in oxidation number. Different sets of rules have been developed to assign oxidation numbers to monatomic ions and to each individual atom in polyatomic molecules. One set of rules is simple and especially easy to use. It can be used to determine the oxidation number of atoms in many, but not all, chemical species. In this set, the rules for assigning oxidation numbers are listed in order by priority of application; the rule written first in the list has priority over the rule below it. The rules are applied in the order in which they come in the list, starting at the top and proceeding down the list of rules until each atom of each element, not the element only, in a species has been assigned an oxidation number. Generally, all atoms of each element in a chemical species will have the same oxidation number in that species. For example, all oxygen in sulfate are -2. (A specific exception is nitrogen in the cation and anion in ammonium nitrate, NH_4NO_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. 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 Group IA elements, Li, Na, K, Rb, Cs, and Fr) have an oxidation number of +1; the alkaline earth metals (the Group IIA elements, Be, Mg, Ca, Sr, Ba, and Ra) have an oxidation number of +2.

3. Fluorine has an oxidation number of −1; hydrogen has an oxidation number of +1.

4. Oxygen has an oxidation number of −2.

5. The halogens (the Group 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 Group VIA elements, O, S, Se, Te, and Po) is −2; for the nitrogen family of elements (the VA elements except 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 Pu^{+4} is +4. Applying rule one again, the charge is +4.

3. The oxidation numbers of carbon and oxygen in 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 the net charge on the molecule is zero. 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 $C + 2(-2) = 0$, 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.

4. The oxidation numbers of calcium and hydrogen in calcium hydride (CaH_2) are +2 and −1, respectively. The compound is neutral, and the application of rule one requires that the oxidation numbers of all atoms add up to 0. By rule two, the oxidation number of calcium is +2. Applying rule one, the oxidation number of hydrogen is: $2H + 2=0$, or −1. Notice that in this example, the oxidation number as predicted by the rules does not agree with rule three, but the number is determined by rules one and two, which take precedence over rule three.

5. The oxidation numbers of uranium and oxygen in the uranyl ion, UO_2^{+2}, are +6 and −2, respectively. Applying rule one, the oxidation numbers of each atom must add up to the

charge of +2. Rule four indicates that the oxygen atoms are −2 each. Applying rule one, the oxidation number of uranium is U + 2(−2) = +2, and uranium is +6. In this example, the charges on uranium and oxygen are not actually +6 and −2, respectively, because the polyatomic ion is held together through covalent bonds. The charge on the ion is the result of a deficiency of two electrons.

Oxidation numbers (states) are commonly represented by zero and positive and negative numbers, such as +4, −2, etc. They are sometimes represented by Roman numerals for metals, especially the oxidation numbers of atoms participating in covalent bonds or those of polyatomic ions, such as chromium(VI) in CrO_4^{-2}. In general, elements in solution whose oxidation number is greater than +4 or less than -4 can exist only as complexed ions in solution. Many of the transuranic elements can occur in multiple oxidation states, and the transformation from one to another is a critical step of the separation process. In this chapter, all species whose oxidation number is greater than +4 will be represented either by their complexed form in solution or by its symbol with a Roman numeral signifying the oxidation state [UO_2^+ or U(V)]. This conforms to the intent of IUPAC (1990) nomenclature.

14.2.3 Common Oxidation States

The oxidation state for any element in its free state (when not combined with any other element, as in Cl_2 or Ag metal) is zero. The oxidation state of a monatomic ion is equal to the electrical charge of that ion. The Group IA elements form ions with a single positive charge (Li^{+1}, Na^{+1}, K^{+1}, Rb^{+1}, and Cs^{+1}), whereas the Group IIA elements form +2 ions (Be^{+2}, Mg^{+2}, Sr^{+2}, Ba^{+2}, and Ra^{+2}). The halogens generally form −1 ions (F^{-1}, Br^{-1}, Cl^{-1}, and I^{-1}); however, except for fluorine, the other halogens form oxygen compounds in which several other oxidation states are present [Cl(I) in HClO and I(V) in HIO_3]. For example, iodine can exist as I^{-1}, I_2, IO^{-1}, IO_3^{-1}, and IO_4^{-1}. Oxygen exhibits a −2 oxidation state except when it is bonded to fluorine (where it can be +1 or +2); in peroxides, where the oxidation state is −1; or in superoxides, where it is -½.

Some radionuclides, such as those of cesium and thorium, exist in solution in single oxidation states, as indicated by their position in the periodic table. Others, such as technetium and uranium, can exist in multiple oxidation states. Multiple oxidation states of plutonium are commonly found in the same solution.

Each of the transition metals has at least two stable oxidation states, except for Sc, Y, and La (Group IIIB), which exhibit only the +3 oxidation state. Generally, negative oxidation states are not observed for these metallic elements. The large number of oxidation states exhibited by the transition elements leads to an extensive, often complicated, oxidation-reduction chemistry. For example, oxidation states from −1 through +7 have been observed for technetium, although the +7 and +4 are most common (Anders, 1960). In an oxidizing environment, Tc exists predominantly in the heptavalent state as the pertechnetate ion, TcO_4^{-1}, which is water soluble, but which can yield insoluble salts with large cations. Technetium forms volatile heptoxides and acid-insoluble heptasulfides. Subsequently, pertechnetate is easily lost upon evaporation of acid solutions unless a reducing agent is present or the evaporation is conducted at low temperatures. Technetium(VII) can be reduced to lower oxidation states by reducing agents such as bisulfite (HSO_3^{-1}). This process proceeds through several intermediate steps, some of which are slow; therefore, unless precautions are taken to maintain technetium in the appropriate oxidation state, erratic results can occur. The (VII) and +4 ions behave very differently in solution. For instance, pertechnetate does not coprecipitate with ferric hydroxide, while Tc^{+4} does.

The oxidation states of the actinide elements have been comprehensively discussed by Ahrland (1986) and Cotton and Wilkinson (1988). The actinides exhibit an unusually broad range of oxidation states, of from +2 to +7 in solution. Similar to the lanthanides, the most common oxidation state is +3 for actinium, americium, and curium. The +4 state is common for thorium and plutonium, whereas (V) is most common for protactinium and neptunium. The most stable state for uranium is the (VI) oxidation state.

In compounds of the +3 and +4 oxidation states, the elements are present as simple M^{+3} or M^{+4} cations (where "M" is the metal ion); but for higher oxidation states, the most common forms in compounds and in solution are the oxygenated actinyl ions, MO_2^{+1} and MO_2^{+2}:

- M^{+3}. The +3 oxidation state is the most stable condition for actinium, americium, and curium, and it is easy to produce Pu^{+3}. This stability is of critical importance to the radiochemistry of plutonium. Many separation schemes take advantage of the fact that Pu can be selectively maintained in either the +3 or +4 oxidation state. Unlike Pu and Np, U^{+3} is such a strong reducing agent that it is difficult to keep in solution.

- M^{+4}. The only oxidation state of thorium that is experienced in radiochemical separations is +4. Pa^{+4}, U^{+4}, and Np^{+4} are stable, but they are easily oxidized by O_2. In acid solutions with low plutonium concentrations, Pu^{+4} is stable. Americium and curium can be oxidized to the +4 state with strong oxidizing agents such as persulfate.

- M(V). The actinides, from protactinium through americium, form MO_2^{+1} ions in solution. PuO_2^{+1} can be the dominant species in solution at low concentration in natural waters that are relatively free of organic material.

- M(VI). This is the most stable oxidation state of uranium, which exist as the UO_2^{+2} species. Neptunium, plutonium, and americium also form MO_2^{+2} ions in solution. The bond strength, as well as the chemical stability toward reduction for these MO_2^{+2} ions, decrease in the order U > Np > Pu > Am.

Reactions that do not involve making or breaking bonds, $M^{+3} \rightarrow M^{+4}$ or $MO_2^{+1} \rightarrow MO_2^{+2}$, are fast and reversible, while reactions that involve chemical bond formation, $M^{+3} \rightarrow MO_2^{+1}$ or $M^{+4} \rightarrow MO_2^{+2}$, are slow and irreversible.

Plutonium exhibits redox behavior unmatched in the periodic table. It is possible to prepare solutions of plutonium ions with appreciable concentrations of four oxidation states, +3, +4, (V), and (VI), as Pu^{+3}, Pu^{+4}, PuO_2^{+1}, and PuO_2^{+2}, respectively. Detailed discussions can be found in Cleveland (1970), Seaborg and Loveland (1990), and in Coleman (1965). According to Cleveland (1970), this polyvalent behavior occurs because of the tendency of Pu^{+4} and Pu(V) to disproportionate:

$$3\ Pu^{+4} + 2\ H_2O \rightarrow 2\ Pu^{+3} + PuO_2^{+2} + 4H^{+1}$$

$$3\ PuO_2^{+1} + 4\ H^{+1} \rightarrow Pu^{+3} + 2\ PuO_2^{+2} + 2\ H_2O$$

and because of the slow rates of reaction involving formation or rupture of Pu-O bonds (such as PuO_2^{+} and PuO_2^{2+}) compared to the much faster reactions involving only electron transfer. The distribution depends on the type and concentration of acid used for dissolution, the method of solution preparation, and the initial concentration of the different oxidation states. In HCl, HNO_3, and $HClO_4$, appreciable concentrations of all four states exist in equilibrium. Seaborg and Loveland (1990) report that in 0.5 M HCl at 25 °C, the equilibrium percentages of plutonium in the various oxidation states are found to be as follows:

Pu^{+3}	27.2%
Pu^{+4}	58.4%
Pu(V)	~0.7%
Pu(VI)	13.6%

Apart from the disproportionation reactions, the oxidation state of plutonium ions in solution is affected by its own decay radiation or external gamma and X-rays. At high levels, radiolysis products of the solution can oxidize or reduce the plutonium, depending on the nature of the solution and the oxidation state of plutonium. Therefore, the stated oxidation states of old plutonium solutions, particularly old $HClO_4$ and H_2SO_4 solutions, should be viewed with suspicion. Plutonium also tends to hydrolyze and polymerize in solution, further complicating the situation (see Section 14.10, "Analysis of Specific Radionuclides").

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

TABLE 14.1 — Oxidation states of elements

Element	Oxidation State(1)	Chemical Form	Notes(2)
Am	**+3**	Am^{+3}	Pink; stable; difficult to oxidize
	+4	Am^{+4}	Pink-red; unstable in acid
	(V)	AmO_2^{+1}	Pink-yellow; disproportionates in strong acid; reduced by products of its own radiation
	(VI)	AmO_2^{+2}	Rum color; stable

Element	Oxidation State(1)	Chemical Form	Notes(2)
Cs	+1	$Cs(H_2O)_x^{+1}$	Colorless; x probably is 6
Co	**+2**	$Co(H_2O)_6^{+2}$	Pink to red; oxidation is very unfavorable in solution
	+3	$Co(H_2O)_6^{+3}$	Rapidly reduced to +2 by water unless acidic
Fe	+2	$Fe(H_2O)_6^{+2}$	Green
	+3	$Fe(H_2O)_6^{+3}$	Pale yellow; hydrolyses in solution to form yellow or brown complexes
^3H	+1	^3HOH and $^3HOH_2^{+1}$	Isotopic exchange of tritium is extremely rapid in samples that have water introduced.
I	**−1**	I^{-1}	Colorless
	-1/3	I_3^{-1}	Brown; commonly in solutions of I^{-1} exposed to air
	+1	OI^{-1}	Colorless
	(V)	IO_3^{-1}	Colorless; formed in vigorously oxidized solutions
	(VII)	IO_4^{-1}	Colorless
Ni	+2	$Ni(H_2O)_6^{+2}$	Green
Nb	+3	Unknown	In sulfuric acid solutions of Nb_2O_5
	+5	$HNb_6O_{19}^{-7}$	
Po	+4		
Pu	+3	$Pu(H_2O)_x^{+3}$	Violet to blue; stable to air and water; easily oxidized to +4
	+4	$Pu(H_2O)_x^{+4}$	Tan to brown; first state formed in freshly prepared solutions; stable in 6 M acid; disproportionates in low acidity to +3 and +6
	(V)	$Pu(H_2O)_x^{+5}$ or PuO_2^{+1}	Never observed alone; always disproportionates; most stable in low acidity Purple
	(VI)	PuO_2^{+2}	Yellow-pink; stable but fairly easy to reduce
	(VII)	PuO_5^{-3} or $PuO_4(OH)_2^{-3}$	Green $PuO_4(OH)_2^{-3}$ more likely form
Ra	+2	$Ra(H_2O)_x^{+2}$	Colorless; behaves chemically like Sr and Ba
Sr	+2	$Sr(H_2O)_x^{+2}$	Colorless
Tc	+4	TcO_3^{-2}	
	(V)	TcO_3^{-1}	
	(VII)	TcO_4^{-1}	
Th	+4	$Th(H_2O)_8^{+4}$	Colorless; at pH>3 forms complex hydrolysis products
U	+3	$U(H_2O)_x^{+3}$	Red-brown; slowly oxidized by water and rapidly by air to +4
	+4	$U(H_2O)_{8\text{ or }9}^{+4}$	Green; stable but slowly oxidized by air to (VI)
	(V)	UO_2^{+1}	Unstable but more stable at pH 2-4; disproportionates to +4 and (VI)
	(VI)	$UO_2(H_2O)_5^{+2}$	Yellow; only form stable in solution containing air; difficult to reduce
Zr	+4	$Zr(H_2O)_6^{+4}$	Only at very low ion concentrations and high acidity
		$Zr_4(OH)_8(H_2O)_{16}^{+2}$	At typical concentrations in absence of complexing agents

(1) Most common form is in bold.

(2) Color shades may vary depending on the concentration of the isotope.

Sources: Booman and Rein, 1962; Cotton and Wilkinson, 1988; Emsley, 1989; Greenwood and Earnshaw, 1984; Grinder, 1962; Hampel, 1968; Katzin, 1986; Latimer, 1952; and 1970.

TABLE 14.2 — Oxidation states of selected elements

Element	+1	+2	+3	+4	V	VI	VII	VIII
Titanium		○	○	●				
Vanadium		○	○	●	●			
Chromium		●	●	○	○	●		
Manganese		●	○	●	○	○	●	
Iron		●	●	○		○		
Cobalt		●	●					
Nickel		●	○	○				
Strontium		●						
Yttrium			●					
Molybdenum		○	○	●	●	●		
Technetium		○	○	●	○	○	●	
Silver	●		○	○				
Cesium	●							
Barium		●						
Lanthanides			●					
Lead		●		○				
Polonium		○		●		○		
Radium		●						
Actinium			●					
Thorium				●				
Protactinium				○	●			
Uranium			○	○	○	●		
Neptunium			○	○	●	○	○	
Plutonium			○	●	○	○		
Americium			●	○	○	○		
Curium			●	○				

The stable nonzero oxidation states are indicated. The more common oxidation states are indicated by solid black circles.
Sources: 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_2 and H_2O_2, 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_2^{+1}, for example, is represented by the chemical equation:

$$2\ UO_2^{+1} + 4\ H^{+1} \rightleftharpoons U^{+4} + UO_2^{+2} + 2\ H_2O \quad (K = 1.7\times10^6)$$

The magnitude of the equilibrium constant reflects the instability of the (V) oxidation state of uranium in UO_2^{+1} described in Table 14.1, and the presence of hydrogen ions reveals the influence of acidity on the redox process. An increase in acidity promotes the reaction.

14.2.5 Common Oxidizing and Reducing Agents

HYDROGEN PEROXIDE. Hydrogen peroxide (H_2O_2) has many practical applications in the laboratory. It is a very strong oxidizing agent that will spontaneously oxidize many organic substances, and water samples are frequently boiled with peroxide to destroy organic compounds before separation procedures. When hydrogen peroxide serves as an oxidizing reagent, each oxygen atom changes its oxidation state from −1 to −2. For example, the reaction for the oxidation of ferrous ion is as follows:

$$H_2O_2 + 2H^{+1} + 2Fe^{+2} \rightleftharpoons 2H_2O + 2Fe^{+3}$$

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

$$4\ H_2O_2 + Tc^{+4} \rightleftharpoons TcO_4^{-1} + 4H_2O$$

Hydrogen peroxide can also serve as a reducing agent, with an increase in oxidation state from -1 to 0, and the liberation of molecular oxygen. For example, hydrogen peroxide will reduce permanganate ion (MnO_4^{-1}) in basic solution, forming a precipitate of manganese dioxide:

$$2\ MnO_4^{-1} + 3\ H_2O_2 \rightarrow 2\ MnO_2\downarrow + 3\ O_2\uparrow + 2\ H_2O + 2\ OH^{-1}$$

Furthermore, hydrogen peroxide can decompose by the reaction:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

This reaction is another example of a disproportionation (auto-oxidation-reduction) in which a chemical species acts simultaneously as an oxidizing and reducing agent; half of the oxygen atoms are reduced to O^{-2}, and the other half are oxidized to elemental oxygen (O^0) in the diatomic state, O_2.

OXYANIONS. Oxyanions (NO_3^{-1}, $Cr_2O_7^{-2}$, ClO_3^{-1}, and MnO_4^{-1}) differ greatly in their oxidizing strength, but they do share certain characteristics. They are stronger oxidizing agents in acidic rather than basic or neutral conditions, and they can be reduced to a variety of species depending on the experimental conditions. For example, on reduction in acidic solutions, the permanganate ion accepts five electrons, forming the manganous ion Mn^{+2}:

$$MnO_4^{-1} + 5\ e^{-1} + 8\ H^{+1} \rightarrow Mn^{+2} + 4\ H_2O$$

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

$$MnO_4^{-1} + 3\ e^{-1} + 4\ H^{+1} \rightarrow MnO_2 \downarrow + 2\ H_2O$$

These oxidizing agents are discussed further in Section 13.4, "Wet Ashing and Acid Dissolution Techniques."

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

PERCHLORIC ACID. The use of perchloric acid ($HClO_4$) as an oxidizing agent is covered in depth in Section 13.4, "Wet Ashing and Acid Dissolution Techniques."

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

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

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

SULFAMIC ACID. Aqueous solutions of this solid material are strongly acidic and act selectively as oxidizing agents. It is of particular value in its ability to oxidize nitrites to nitrates while not affecting Pu^{+3} or Np^{+4} ions.

14.2.6 Oxidation State and Radiochemical Analysis

Most radiochemical analyses require the radionuclide be in aqueous solution. Thus, the first step of an analysis is the complete dissolution of the sample, so that all components remaining at the end of the process are in a true solution, and chemical equilibration with tracers or carriers can be established. Dissolution of many samples requires vigorous conditions to release the radionuclides from its natural matrix. Strong mineral acids or strong bases, which also serve as powerful oxidizing agents, are used in boiling mixtures or under fusion conditions to decompose the matrix—evaporating portions of the acid or base from the mixture and oxidizing the radionuclide to a common oxidation state. The final state depends, generally, on the radionuclide, oxidizers used, and pH of the solution (see notes to Table 14.1, page 14-9). Even water samples might contain radionuclides at various states of oxidation because of their exposure to a variety of natural oxidizing conditions in the environment and the pH of the sample.

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

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

TABLE 14.3 — Redox reagents for radionuclides(1)

Redox Reaction	Reagent	Conditions
$Am^{+3} \rightarrow AmO_2^{+2}$	Ag^{+2}, $Ag^{+}/S_2O_8^{-2}$	
$Am^{+4} \rightarrow AmO_2^{+2}$	O_3	13 M NH_4F
$AmO_2^{+1} \rightarrow AmO_2^{+2}$	Ce^{+4}	$HClO_4$
	O_3	Heated HNO_3 or $HClO_4$
$AmO_2^{+2} \rightarrow AmO_2^{+1}$	Br^{-1}, Cl^{-1}	
	Na_2CO_3	Heat to precipitate $NaAmO_2CO_3$; dissolve in H^{+1}
$AmO_2^{+2} \rightarrow Am^{+3}$	I^{-1}, H_2O_2, NO_2^{-1}, SO_2	
$Am^{+4} \rightarrow Am^{+3}$	alpha radiation effects	Spontaneous
$Co^{+2} \rightarrow Co^{+3}$	O_3	Cold $HClO_4$
	O_2, H_2O_2	Complexed cobalt
$Co^{+3} \rightarrow Co^{+2}$	H_2O	Rapid with evolution of H_2
$Fe^{+2} \rightarrow Fe^{+3}$	O_2	Faster in base; slower in neutral and acid solution; decreases with H^{+1}
	Ce^{+4}, MnO_4^{-1}, NO_3^{-1}, H_2O_2, $S_2O_8^{-2}$	
	$Cr_2O_7^{-2}$	HCl or H_2SO_4

Redox Reaction	Reagent	Conditions
$Fe^{+3} \rightarrow Fe^{+2}$	H_2S, H_2SO_3	Excess removed by boiling
	Zn, Cd, Al, Ag amalgams	
	Sn^{+2}, I^{-1}, Cu^{+1}, Ti^{+3}	
	NH_2OH	Boiling solution
$I^{-1} \rightarrow I_2$	HNO_2 ($NaNO_2$ in acid)	Does not affect other halides
	MnO_2 in acid	Well suited for lab work
	6M HNO_3	
	$NaHSO_3$ or $NaHSO_3$ in H^{+1}	
	Na_2SO_3; $Na_2S_2O_3$	
$I^{-1} \rightarrow IO_3^{-1}$	$KMnO_4$	
	50% CrO_3 in 9M H_2SO_4	
$I^{-1} \rightarrow IO_4^{-1}$	NaClO in base	
$IO_4^{-1} \rightarrow I_2$	$NH_2OH{\cdot}HCl$	
	$H_2C_2O_4$	9 M H_2SO_4
$IO_4^{-1} \rightarrow I^{-1}$	$NaHSO_3$ in acid	
$I_2 \rightarrow I^{-1}$	SO_2; $NaHSO_3$	
$Np^{+3} \rightarrow Np^{+4}$		Dilute acid
$Np^{+4} \rightarrow NpO_2^{+1}$	NO_2^{-1}	HNO_3
$Np^{+4} \rightarrow NpO_2^{+2}$	MnO_4^{-1}	Dilute alkaline
$NpO_2^{+1} \rightarrow NpO_2^{+2}$		Acid
$NpO_2^{+2} \rightarrow NpO_5^{-3}$		Acid
$NpO_2^{+1} \rightarrow Np^{+4}$	Fe^{+2}	Dilute H_2SO_4
	Ti^{+3}	1–2 M HCl
$Pu^{+3} \rightarrow Pu^{+4}$	BrO_3^{-1}	Dilute H^{+1}
	Ce^{+4}	HCl or H_2SO_4 solution
	$Cr_2O_7^{-2}$, IO_3^{-1}, MnO_4^{-1}	Dilute H^{+1}
	NO_2^{-1}	HNO_3
	NO_3^{-1}	HNO_3 or dilute HCl (100°C)
	HNO_2	
$Pu^{+4} \rightarrow PuO_2^{+2}$	$NaBiO_3$	HNO_3
	BrO_3^{-1}	Dilute HNO_3 at 85°C
	Ce^{+4}	Dilute HNO_3 or $HClO_4$
	HOCl (KClO)	pH 4.5 at 80°C or 45% K_2CO_3 at 40°C
	MnO_4^{-1}	Dilute HNO_3
	O_3	Ce^{+4} or Ag^{+1} catalyst or dilute H_2SO_4/60°C
	Ag^{+2}	$Ag^{+1}/S_2O_8^{-1}$ in dilute HNO_3
	$Cr_2O_7^{-2}$	Dilute H_2SO_4
	Cl_2	Dilute H_2SO_4 at 80°C or dil.$HClO_4/Cl^{-1}$
	NO_3^{-1}	Dilute HNO_3 at 95°C
	Ag_2O	43% K_2CO_3 at 75°C
	IO_3^{-}	
$PuO_2^{+1} \rightarrow PuO_2^{+2}$	HNO_3	Dilute; slow
	V^{+3} or Ti^{+3}	$HClO_4$; slow
$PuO_2^{+2} \rightarrow PuO_2^{+1}$	I^{-1}	pH 2
	SO_2	H^{+1}

Redox Reaction	Reagent	Conditions
	Fe^{+2}	$HClO_4$ or HCl
	V^{+3} or U^{+4}	$HClO_4$
	HNO_2	Dilute HNO_3NaNO_3
	Ag	Dilute HCl
$PuO_2^{+2} \rightarrow Pu^{+4}$	$C_2O_4^{-2}$	75 °C; RT with dilute HCl
	I^{-1}	HNO_3
	Fe^{+2}	HCl, HNO_3, or H_2SO_4
	Sn^{+2}	$HCl/HClO_4$
	H_2O_2	HNO_3; continues to Pu^{+3} in absence of Fe^{+3}
	Ti^{+3}	$HClO_4$
	Cu_2O	45% K_2CO_3 75 °C
	HNO_2	HNO_3/75 °C
	Zn	Dilute HCl
$PuO_2^{+1} \rightarrow Pu^{+4}$	HNO_2	Slow
	$NH_2OH \cdot HCl$	Dilute HCl, slow
$Pu^{+4} \rightarrow Pu^{+3}$	hydroquinone	Dilute HNO_3
	H_2/Pt	HCl
	I^{-1}	Dilute HCl
	HSO_3^{-1}	Dilute HNO_3
	$NH_2OH \cdot HCl$	
	Zn	Dilute HCl
	SO_2	Dilute HNO_3
	Ti^{+3}	HCl, dilute H_2SO_4, or dilute HNO_3/H_2SO_4
	ascorbic acid	HNO_3
	U^{+4}	Dilute $HClO_4$
	H_2S	Dilute acid
$Tc^{+4} \rightarrow TcO_4^{-1}$	HNO_3	
	H_2O_2	
	O_2 (air)	
TcO_2(hydrated) → TcO_4^{-1}	Ce^{+4}	
	H_2O_2	
$TcCl_6^{-2} \rightarrow TcO_4^{-1}$	H_2O_2	
	Cl_2	
	Ce^{+4}	
	MnO_4^{-1}	
$TcO_4^{-1} \rightarrow Tc^{+4}$ or TcO_2(hyd)	N_2H_4	Dilute H_2SO_4
	NH_2OH	Dilute H_2SO_4
	Ascorbic acid	Dilute H_2SO_4
	Sn^{+2}	Dilute H_2SO_4
	Zn	Dilute HCl
	Concentrated HCl	$\rightarrow TcCl_6^{-2}$
$U^{+3} \rightarrow U^{+4}$	ClO_4^{-1}	Dilute $HClO_4$
	Co^{+3} complexes	Dilute $HClO_4$ or $LiClO_4$

Redox Reaction	Reagent	Conditions
	Cr^{+3} and Cr^{+3} complexes	Dilute $HClO_4$ or $LiClO_4$
	H_2O	Dilute or concentrated HCl or H_2SO_4
	O_2 (air)	
$U^{+4} \rightarrow UO_2^{+2}$	Br_2	Catalyzed by Fe^{+3} or Mn^{+2}
	BrO_3^{-1}	$HClO_4$
	Ce^{+4}	Dilute $HClO_4$
	ClO_3^{-1}	Catalyzed by Fe^{+2} or V^{+5}
	Fe^{+3}	
	$HClO_2$	Phenol
	$HCrO_4^{-1}$	
	HNO_2	Catalyzed by Fe^{+2}
	HNO_3	
	H_2O_2	
	O_2	
	MnO_2	
$UO_2^{+1} \rightarrow UO_2^{+2}$	Fe^{+3}	
$UO_2^{+2} \rightarrow U^{+4}$	Cr^{+2}	
	Eu^{+2}	
	Np^{+3}	
	Ti^{+3}	
	V^{+2} and V^{+3}	
	Rongalite (an aqueous solution of sodium hydroxymethanesulfonate)	Dilute basic solution
$UO_2^{+2} \rightarrow U^{+3}$	Zn(Hg)	
$UO_2^{+1} \rightarrow U^{+4}$	Cr^{+2}	
	H_2	
	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.

One method for the analysis of radioiodine in aqueous solutions illustrates the use of oxidation and reduction chemistry to bring the radionuclide to a specific oxidation state so that it can be isolated from other radionuclides and other elements (DOE, 1997, Method RP230). Iodine species in the water sample are first oxidized to iodate (IO_4^{-1}) by sodium hypochlorite (NaClO), and then reduced to iodide (I^{-1}) by sodium bisulfite. The iodine is finally oxidized to molecular iodine (I_2) and extracted from most other radionuclides and elements in solution by a nonpolar organic solvent such as carbon tetrachloride (CCl_4) or chloroform ($CHCl_3$) (see Section 14.4, "Solvent Extraction").

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

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

The classical titrimetric method is not commonly employed in the quantitation of environmental level samples because the concentrations of radionuclides in these samples are typically too low for detection of the endpoint of the titration, even by electrometric or spectroscopic means. However, the method is used for the determination of radionuclides in other samples containing larger quantities of long-lived radionuclides. Millimole quantities of uranium and plutonium in nuclear fuels have been determined by titration using methods of endpoint detection as well as chemical indicators (IAEA, 1972). In one method, uranium in the (VI) oxidation state is first reduced to +3 and +4 with Ti^{+3}, then uranium in the +3 state is oxidized to +4 with air bubbles (Baetsel and Demildt, 1972). The solution is then treated with a slight excess of Ce^{+4} solution of known concentration, which oxidizes U^{+4} to U(VI) (as UO_2^{+2}) while being reduced, as follows:

$$U^{+4} + 2\,Ce^{+4} \rightarrow U^{+6} + 2\,Ce^{+3}$$

$$(U^{+4} + 2\,Ce^{+4} + 2\,H_2O \rightarrow UO_2^{+2} + 2\,Ce^{+3} + 4\,H^{+1})$$

The excess Ce^{+4} is back-titrated with Fe^{+2} solution, using ferroin as indicator for the endpoint of the titration:

$$Fe^{+2} + Ce^{+4} \rightarrow Fe^{+3} + Ce^{+3}$$

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

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

Oxidation-reduction chemistry often is used to separate mixtures of transuranics. This is because mixtures of several transuranics (e.g., U, Pu, Cm) or transition metals will generate different oxidation states of each element as a result of inter-element redox reactions. An example would be :

$$2\ H_2O\ +\ U^{+4}\ +\ 2\ Pu^{+4} \rightarrow UO_2^{2+}\ +\ 2\ Pu^{+3}\ +\ 4\ H^+$$

Thus, when attempting to determine plutonium (as the Pu^{+4} ion) in a solution containing U^{+4}, it would be necessary to isolate most of the plutonium from the uranium before Pu^{+4} can be analyzed successfully. The isolation would take place using extraction, precipitation, or chromatographic methods.

14.3 Complexation

14.3.1 Introduction

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

$$Th^{+4} + 2\ NO_3^{-1} \rightarrow Th(NO_3)_2^{+2}$$

$$Ra^{+2} + EDTA^{-4\,*} \rightarrow Ra(EDTA)^{-2}$$

$$U^{+4} + 5\ CO_3^{-2} \rightarrow U(CO_3)_5^{-6}$$

* $EDTA^{-4}$ = Ethylene diamine tetraacetate, $^{-1}(OOC)_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}(COO)_2^{-1}$

In a fundamental sense, every ion in solution can be considered complexed; there are no free or “naked” ions. Dissolved ions are surrounded by solvent molecules. In aqueous solutions, the complexed water molecules, referred to as the inner hydration sphere, form aquo ions that can be either weakly or strongly bound:

$$Fe^{+2} + 6\ H_2O \rightarrow Fe(H_2O)_6^{+2}$$

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

$$M(H_2O)_n^{+x} + L^{-y} \rightarrow M(H_2O)_{n-1}L^{x-y} + H_2O$$

Successive aquo groups can be replaced by other ligand groups until the complex ML_n^{x-ny} is formed as follows:

$$M(H_2O)_{n-1}\,L^{x-y} + L^{-y} \rightarrow M(H_2O)_{n-2}\,L_2^{x-2y} + H_2O, \text{ etc.}$$

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

Ligands are classified by the number of electrons they donate to the metal to form coordination bonds to the metal. If only one atom in the ligand is bonded to the metal, it is called a "unidentate ligand" (from the Latin word for teeth). It is a categorization of ligands that describe the number of atoms with electron pairs a ligand has available for donation in complex-ion formation; if two atoms, bidentate, and so on for tridentate, tetradentate, pentadentate, and hexadentate. The term "coordination number" is also used to indicate the number of atoms donating electrons to the metal atom. The coordination number is 10 in $U(CO_3)_5^{-6}$, as illustrated above. EDTA, also illustrated above, is a hexadentate ligand, because it bonds to the metal through the four oxygen atoms and two nitrogen atoms. Table 14.4 lists some common ligands arranged by type.

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 β-diketones generally complex all metals. Conversely, cyanide (CN^{-1}), the heavy halides, sulfur donors, and—to a lesser 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.

TABLE 14.4 — Common ligands

Ligand Type (1)	Examples
Unidentate	Water (H_2O), halides (X^{-1}), hydroxide (OH^{-1}), ammonia (NH_3), cyanide (CN^{-1}), nitrite (NO_2^{-1}), thiocyanate (SCN^{-1}), carbon monoxide (CO)
Bidentate	Oxalate, ethylene diamine, citrate
Tridentate	Diethylene triamine, 1,3,5 triaminocyclohexane
Polydentate	8-hydroxyquinoline, β-diketones (thenoyltrifluoroacetone [TTA]), ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA) Organophosphates: (octyl(phenyl)-*N*,*N*-diiso-butylcarbamoyl-methylphosphine oxide [CMPO]); tributylphosphate (TBP), trioctylphosphinic oxide (TOPO), quaternary amines (tricaprylyl-methylammonium chloride [Aliquat-336®]), triisooctylamine (TIOA), tri-*n*-octylamine (TnOA), macrocyclic polyethers (crown ethers such as [18]-crown-6), cryptates

(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.

14.3.2 Chelates

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 (RCOOH) or amine (RNH_2) functional groups. A chelate is effective at a pH where the acid groups are in the anionic form as carboxylates, $RCOO^{-1}$, 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, 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.

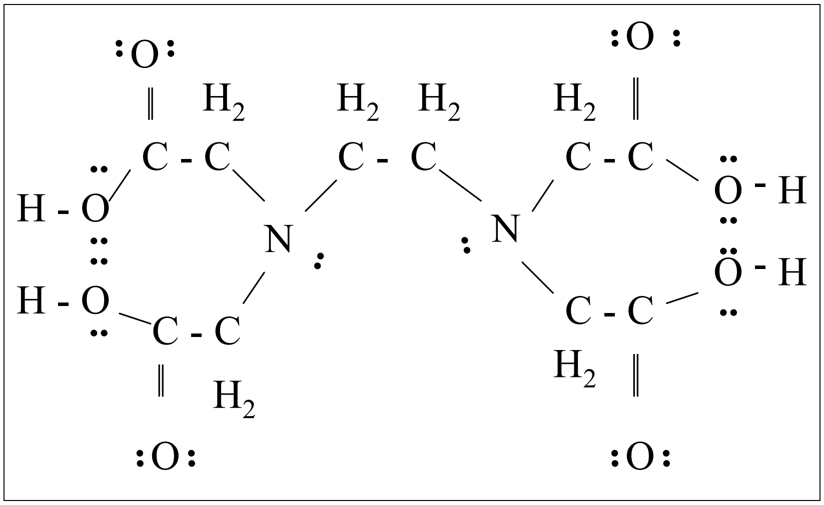
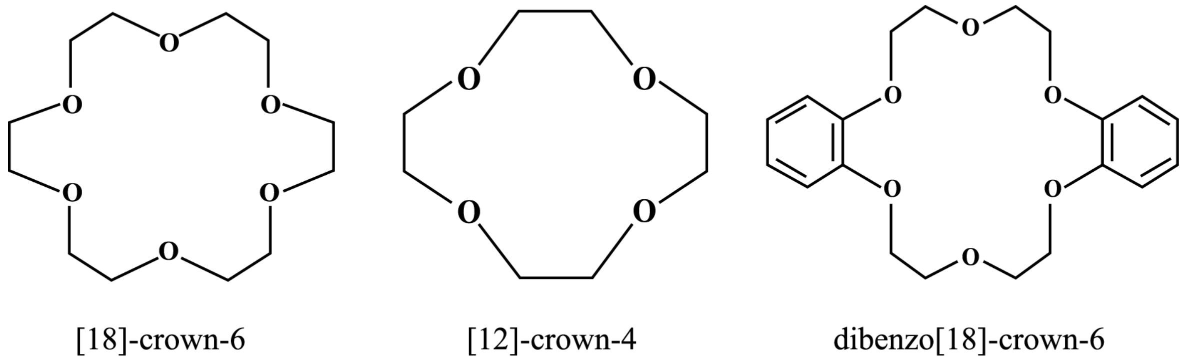


FIGURE 14.1 — Ethylene diamine tetraacetic acid (EDTA)

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

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

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


[18]-crown-6

[12]-crown-4

dibenzo[18]-crown-6

FIGURE 14.2 — Crown ethers

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

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

Other crown ethers are selective for radionuclide ions such as radium and UO_2^{+2}. Addition of 18-crown-6 to solutions containing NpO_2^{+2} causes the reduction of neptunium to Np(V) as NpO_2^{+1}, which is encircled by the ether ligand (Clark et al., 1998).

14.3.3 The Formation (Stability) Constant

The stability of the complex is represented by the magnitude of an equilibrium constant representing its formation. The complex ion, $[Th(NO_3)_2^{+2}]$, forms in two equilibrium steps:

$$Th^{+4} + NO_3^{-1} \rightarrow Th(NO_3)^{+3}$$

$$Th(NO_3)^{+3} + NO_3^{-1} \rightarrow Th(NO_3)_2^{+2}$$

The final equation is:

$$Th^{+4} + 2NO_3^{-} \rightarrow Th(NO_3)_2^{+2}$$

The stepwise formation (stability) constants are:

$$K_1 = \frac{[Th(NO_3)^{+3}]}{[Th^{+4}][NO_3^{-1}]}$$

and

$$K_2 = \frac{[Th(NO_3)_2^{+2}]}{[Th(NO_3)^{+3}][NO_3^{-1}]}$$

The overall formation (stability) constant is:

$$K_f = K_1 \cdot K_2 \frac{[Th(NO_3)_2^{+2}]}{[Th^{+4}][NO_3^{-1}]^2}$$

In the Ni^{+2} examples cited in the preceding section, the relative stabilities of the complex ions are represented by the values of K; for $Ni(en)_3^{+2}$ it is $10^{18.28}$, and for $Ni(NH_3)^{+2}$ it is $10^{8.61}$ (Cotton and Wilkinson, 1988).

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

- Complexation of UO_2^{+2} with carbonate to form $UO_2(CO_3)_3^{-4}$ increases the solubility of the uranium species in groundwater (Lindsay, 1988).

- Thorium (+2) forms $Th(NO_3)_6^{-2}$ in nitric acid solution (optimally at 7 M) that is the basis for separation of thorium from other actinides and thorium progeny, because they do not form anionic complexes under these conditions (Hyde, 1960).

- Radium (+2) forms a very insoluble compound with sulfate ($RaSO_4$) but is soluble in hot concentrated sulfuric acid because of the formation of $Ra(SO_4)_2^{-2}$ (Kirby and Salutsky, 1964).

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

14.3.4 Complexation and Radiochemical Analysis

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

14.3.4.1 Extraction of Laboratory Samples and Ores

Uranium ores are leached with alkaline carbonates to dissolve uranium as the $UO_2(CO_3)_3^{-4}$ complex ion after oxygen is used to convert U^{+4} to U(VI) (Grindler, 1962). Samples containing refractory plutonium oxides are dissolved with the aid of a nitric acid-hydrofluoric acid solution to produce the complex cation PuF^{+3} and similar cationic fluorocomplexes (Booman and Rein, 1962). Refractory silicates containing niobium (Nb) also yield to fluoride treatment. Potassium bifluoride (KF_2^{-1}) is used as a low-temperature flux to produce a fluoride complex NbF_6^{-1} (Willard and Rulfs, 1961; Greenwood and Earnshaw, 1984).

14.3.4.2 Separation by Solvent Extraction and Ion-Exchange Chromatography

Many ion-exchange separations of radionuclides are based on the formation of complex ions from the metal ions in solution or the displacement of ions bound to an exchanger by complex formation. Uranium in urine samples, for example, is partly purified by forming a chlorocomplex of U^{+4} and UO_2^{+2} ions, UCl_6^{-2} and $UO_2Cl_3^{-1}$, that bind preferentially to the anion-exchange ligands in 7 M HCl. Other cations pass through the column under these conditions. Uranium is subsequently eluted with 1 M HCl (DOE, 1990 and 1997, Method U-01).

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

Thorium (+4) is bound more strongly to cation exchangers than most other cations (Hyde, 1960). The bound thorium is separated from most other ions by washing the column with mineral acids or other eluting agents. Even the tetrapositive plutonium ion, Pu^{+4}, and the uranyl ion, UO_2^{+2}, are washed off with high concentrations of HCl because they form chlorocomplexes, $PuCl_6^{-2}$ and $UO_2Cl_3^{-1}$, respectively. Thorium is then removed by eluting with a suitable complexing agent such as oxalate, which reduces the effective concentration of Th^{+4}, reversing the exchange process. Using oxalate, $Th(C_2O_4)_4^{-4}$ forms and the anion is not attracted to the cation exchanger.

14.3.4.3 Formation and Dissolution of Precipitates

A classical procedure for the separation and determination of nickel (Ni) is the precipitation of Ni^{+2} with dimethylglyoxime, a bidentate ligand that forms a highly selective, stable chelate complex with the ion, $Ni(C_4H_7N_2O_2^{-1})_2$ (DOE, 1997, Method RP300). Uranium in the +4 oxidation state can also be precipitated from acidic solutions with a chelating agent, cupferron (ammonium nitrosophenylhydroxylamine, $C_8H_5(NO)O^{-1}NH_4^{+1}$) (Grindler, 1962). In another procedure, Co^{+2} can be selectively precipitated from solution as $K_3Co(NO_2)_6$. In this procedure, cobalt, which forms the largest number of complexes of all the metals, forms a complex anion with six nitrite ligands, $Co(NO_2)_6^{-3}$ (EPA, 1973).

In radiochemical separations and purification procedures, precipitates of radionuclides are commonly redissolved to release the metal ion for further purification or determination. In the determination of ^{90}Sr, Sr^{+2} is separated from the bulk of the solution by direct precipitation of the sulfate, $SrSO_4$. The precipitate is redissolved by complexation with EDTA, $Sr(EDTA)^{-2}$, to separate it from lanthanides and actinides (DOE, 1997, Method RP520). Radium also forms a very stable complex with EDTA. Solubilization of radium, Ra^{+2}, coprecipitated with barium sulfate ($BaSO_4$) is used in the ^{228}Ra determination of drinking water by using EDTA (EPA, 1980).

14.3.4.4 Stabilization of Ions in Solution

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

14.3.4.5 Detection and Determination

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

Spectrometric determinations are also based on the formation of complex ions. Microgram quantities of uranium are determined by the absorbance at 415 nm (a colorimetric determination) of the uranyl chelate complex with dibenzoylmethane, C_6H_5-CO-CH_2-CO-C_6H_5 (Grindler, 1962).

14.4 Solvent Extraction

14.4.1 Extraction Principles

Solvent extraction has been an important separation technique since the early days of the Manhattan Project, when scientists extracted uranyl nitrate into diethyl ether to purify the uranium used in the first reactors. Solvent extraction, or liquid-liquid extraction, is a technique used both in the laboratory and on the industrial scale. However, current laboratory trends are away from this technique, mainly because of the costs of materials and because it is becoming more difficult and costly to dispose of the mixed waste generated from the large volumes of solvents required. The technique also tends to be labor intensive because of the need for multiple extractions using separatory funnels. Nonetheless, solvent extraction remains a powerful separation technique worthy of consideration.

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

$$A_{aq} \rightleftharpoons A_{org}$$

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

14.4.2 Distribution Coefficient

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

$$K_d = \frac{[A_{org}]}{[A_{aq}]}$$

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

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

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

$$2A_{org} \rightleftarrows (A)_{2,\,org}$$

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

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

or

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

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

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

Substitution of K_d produces:

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

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

14.4.3 Extraction Technique

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

> “In solvent extraction, the element which is to be separated, contained in an aqueous solution, is converted to a compound which is soluble in an organic solvent. The organic solvent must be virtually immiscible with water. By shaking the aqueous solution with the organic solvent (extractant) in a separating funnel, the element is extracted into the organic phase. After allowing the aqueous and organic phases to separate in the funnel, the organic extract is removed from contact with the aqueous layer. This single-stage batch extraction method is

employed when K_d is relatively large and for a simple separation it is essential that the distribution coefficients of the metal ions to be separated be sufficiently different. As in the case of ion exchange, the effectiveness of separation is usually expressed by means of the separation factor which is given by the ratio of the distribution coefficients of two different elements which were determined under identical experimental conditions. This ratio determines the separability of two elements by liquid-liquid extraction. Separations can only be achieved if this ratio shows a value which is different from unity and they are clean and can be quickly and easily achieved where one of the distribution coefficients is relatively large and the other very small (high separation factor).

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

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

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

> "In solvent extraction the specific gravity of the extractant in relation to the aqueous phase is important. The greater the difference in the solvent densities, the faster will be the rate at which the immiscible layers separate. Emulsions are more easily produced when the densities of the two solvents are similar. Sometimes troublesome emulsions can be broken by introducing a strong electrolyte into the system or by the addition of small quantities of an aliphatic alcohol"

Korkisch (1969) continues:

> "Liquid-liquid extraction can be applied to the analysis of inorganic materials in two different ways.
>
> (a) Where the element or elements to be determined are extracted into the organic phase.
>
> (b) Where the interfering elements are removed by extraction, leaving the element or elements to be determined in the aqueous phase.
>
> "Solvent extraction separations are mainly dependent for their successful operation upon the distribution ratio of the species between the organic and aqueous phase and the pH and salt concentration of the aqueous phase. Much of the selectivity which is achieved in liquid-liquid extraction is dependent upon adequate control of the pH of the solution. The addition of masking agents such as EDTA and cyanide can greatly improve selectivity, but they too are dependent upon the pH of the solution to exert their full effect. In many cases complete extractions and separations are obtained only in the presence of salting-out agent. An example is the extraction of uranyl nitrate. In the presence of additional nitrate, the increase in the concentration of the nitrate ion in the aqueous solution shifts the equilibrium between the uranyl ion and the nitrate complexes toward the formation of the latter, and this facilitates a more complete extraction of the uranium into the organic solvent. At the same time, the salting-out agent has another, more general, effect: as its affinity for water is large, it becomes hydrated by the water molecules so that the substance to be extracted is really dissolved in a smaller amount of water, and this is the same as if the concentration in the solution were increased. As a result, the distribution coefficient between the aqueous and the organic phases is increased. As a rule the salting-out agent also lowers the solubility of the extractant in the aqueous phase, and this is often important in separations by extraction. The efficiency of the salting-out action depends upon the nature and the concentration of the salting-out agent. For the same molar concentration of the salting-out agent its action increases with an increase in the charge and decrease in the radius of its cation."

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

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

The radioanalytical procedure for uranium and thorium employs solvent extraction to separate the analytes before alpha counting (EPA, 1984). An aqueous solution of the two is extracted with a 10 percent solution of triisooctylamine (TIOA) in para-xylene to remove uranium, leaving thorium in the water (Grinder, 1962). Each solution is further processed to recover the respective radionuclides for separate counting.

14.4.4 Solvent Extraction and Radiochemical Analysis

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

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

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

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

$$RNH_2 + HCl \rightarrow RNH_3^{+1}Cl^{-1}$$

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

$$RCOOH + NaOH \rightarrow RCOO^{-1}Na^{+1} + H_2O$$

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

A number of organophosphorus compounds are also efficient extractants because they and their complexes are readily soluble in organic solvents. The actinide MO_2^{+2} and actinide +4 ions are very effectively extracted by reagents such as bis(2-ethylhexyl) phosphoric acid (HDEHP) and dibutylphosphoric acid (HDBP) (Cadieux and Reboul, 1996).

Among the neutral compounds, alcohols, ethers, and ketones have been commonly employed as extractants. Methyl isobutyl ketone was used in one of the early large-scale processes (the Redox process) to recover uranium and plutonium from irradiated fuel (Choppin et al., 1995). However, the most widely used neutral extractants are the organophosphorus compounds such as TBP (tributylphosphate). The actinide elements thorium, uranium, neptunium, and plutonium easily form complexes with TBP (Choppin et al., 1995). Salting-out agents such as HNO_3 and $Al(NO_3)_3$ are commonly employed to increase extraction in these systems. This chemistry is the basis of the Purex process used to reprocess spent nuclear fuel (Choppin et al., 1995).

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

The amines, especially the tertiary and quaternary amines, are strong cationic extractants. These strong bases form complexes with actinide metal cations. The extraction efficiency improves when the alkyl groups have long carbon chains, such as in tri-*n*-octylamine (TnOA) or TIOA. The pertechnetate ion (TcO_4^{-1}) is also extracted by these cationic extractants (Chen, 1990).

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

TABLE 14.5 — Radioanalytical methods employing solvent extraction (1)

Analyte	Extraction Conditions (Reference)
$^{89/90}$Sr	From soils and sediments with dicyclohexano-18-crown-6 in trichloromethane with back extraction with EDTA (Pimpl, 1995)
$^{99}TcO_4^-$	From dilute H_2SO_4 solutions into a 5% TnOA in xylene mixture and back extracted with NaOH (Golchert and Sedlet, 1969; Chen, 1990); from dilute H_2SO_4, HNO_3, and HCl solutions into a 5% TnOA in xylene (Dale et al., 1996); from HNO_3 into 30% TnOA in xylene and back extracted with NaOH (Hirano, 1989); from dilute H_2SO_4 solutions into TBP (Holm et al., 1984; Garcia-Leon, 1990); the tetraphenyl arsonium complex of Tc into chloroform (Martin and Hylko, 1987); from K_2CO_3 with methyl ethyl ketone (Paducah R-46); from alkaline nuclear-waste media with crown ethers (Bonnesen et al., 1995)
^{210}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	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)
	And other metals from TOPO (NAS-NS 3102) and from high-molecular weight amines such as TIOA (NAS-NS 3101).
	Uranium and plutonium from HCl with TIOA (Moore, 1958)
	From nitric acid wastes using the TRUEX process with CMPO (Horwitz et al., 1985 and 1987)
	With various extractive scintillators followed by PERALS® spectrometry (McDowell 1986 and 1992); with HDEHP after extraction chromatography followed by PERALS® spectrometry (Cadieux and Reboul, 1996)
Thorium	From aqueous samples after ion exchange with TTA, TIOA, or Aliquat-336® (DOE, 1997, Method RP570)
Uranium	From waters with ethyl acetate and magnesium nitrate as salting-out agent (EPA, 1980, Method 908.1); with URAEX™ followed by PERALS® spectrometry (Leyba et al., 1995)
	From soil, vegetation, fecal ash, and bone ash with Alamine-336 (DOE, 1990 and 1997, Methods Se-01, U-03)

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

14.4.5 Solid-Phase Extraction

A technique closely related to solvent extraction is solid-phase extraction (SPE). SPE is a solvent-extraction system in which one of the phases is made stationary by adsorption onto a solid support, usually silica, and the other liquid phase is mobile. Small columns or membranes are used in the SPE approach. Many of the same extracting agents used in solvent extraction can be used in these systems. SPE is becoming widely accepted as an excellent substitute for liquid-liquid extraction because it is generally faster, more efficient, and generates less waste.

14.4.5.1 Extraction Chromatography Columns

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

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

TABLE 14.6 — Radioanalytical methods employing extraction chromatography (1)

Analyte	Ligand	Method Citations
Ni-59/63	dimethylglyoxime	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 1992a); Water (ASTM, D5811-95; DOE, 1997, 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, 1997, Method RP550)
Pb-210	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in isodecanol	Water (DOE, 1997, Method RP280); Geological materials (Horwitz et al., 1994; Woittiez and Kroon, 1995); complex metal ores (Gale, 1996)
Ra-228	CMPO in tributyl phosphate or HDEHP impregnated in Amberlite XAD-7	Natural waters (Burnett et al., 1995); Volcanic rocks (Chabaux, 1994)

Analyte	Ligand	Method Citations
Rare earths	diamyl,amylphosphonate	Actinide-containing matrices (Carney, 1995)
	CMPO in tributyl phosphate and HDEHP impregnated in Amberlite XAD-7	Sequential separation of light rare earths, U, and Th in geological materials (Pin et al., 1996)
	CMPO in tributyl phosphate and 4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Concomitant separation of Sr, Sm, and Nd in silicate samples (Pin et al., 1994)
Actinides	CMPO in tributyl phosphate	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)
	diamyl,amylphosphonate	Acidic media (Horwitz et al., 1992b)
	tri-*n*-octylphosphine oxide [TOPO] and HDEHP	Environmental and industrial samples (Testa et al., 1995)

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

14.4.5.2 Extraction Membranes

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

These SPE membranes significantly reduce extraction time and reagent use in the processing of large environmental water samples. Samples typically are processed through the membranes at flow rates of at least 50 mL/min; a 1 L sample can be processed in as little as 20 minutes. Moreover, these selective-membranes often can be counted directly, thereby condensing sample preparation and counting source preparation into a single step. Many of the hazardous reagents associated with more traditional methods are eliminated in this approach, and these membrane-based extractions use up to 90 percent less solvent than liquid-liquid extractions. The sorbent particles embedded in the membrane are extremely small and evenly distributed, thereby eliminating the problem of channeling that is associated with columns.

14.4.6 Advantages and Disadvantages of Solvent Extraction

14.4.6.1 Advantages of Liquid-Liquid Solvent Extraction

- Lends itself to rapid and very selective separations that are usually highly efficient.
- Partition coefficients are often approximately independent of concentration down to tracer levels and, therefore, can be applied to a wide range of concentrations.
- Can usually be followed by back-extraction into aqueous solvents or, in some cases, the solution can be used directly in subsequent procedures. This also provides significant pre-analysis concentration of the analyte.
- Wide scope of applications—the composition of the organic phase and the nature of complexing or binding agents can be varied so that the number of practical combinations is virtually unlimited.
- Can be performed with simple equipment, but can also be automated.

14.4.6.2 Disadvantages of Liquid-Liquid Solvent Extraction

- Cumbersome for a large number of samples or for large samples.
- Often requires toxic or flammable solvents.
- Can be time consuming, especially if attainment of equilibrium is slow.
- Can require costly amounts of organic solvents and generate large volumes of organic waste.
- Can be affected by small impurities in the solvent(s).
- Multiple extractions might be required, thereby increasing time, consumption of materials, and generation of waste.
- Formation of emulsions can interfere with the phase-separation process.
- Counter-current process can be complicated and can require complicated equipment.
- Alteration of chemical form can change, going from one phase to the other, thereby altering the distribution coefficient and effectiveness of the extraction.
- Tracer-levels of analytes can form radiocolloids that cannot be extracted, dissociate into less soluble forms, or adsorb on the container surface or onto impurities in the system.

14.4.6.3 Advantages of Solid-Phase Extraction Media

- Column/filter extraction may be unattended.
- Column/filter extraction is very selective.

- Generates a low volume of waste, can often be applied to samples dissolved in very acidic media.
- Requires relatively inexpensive equipment.
- In may cases can be correlated with liquid/liquid extraction.

14.4.6.4 Disadvantages of Solid-Phase Extraction Media

- Extraction columns cannot be reused—a cost factor.
- Any suspended matter may be filtered by the media, carrying contaminants into the next step of the separation or analysis.
- Flow rate through columns are generally slow (1-3 mL/min).

14.5 Volatilization and Distillation

14.5.1 Introduction

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

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

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

14.5.2 Volatilization Principles

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

TABLE 14.7 — Elements separable by volatilization as certain species

H abcd																	He a
Li a	Be											B bc$^+$d	C bcd	N abcd	O abcd	F abcd	Ne a
Na a	Mg											Al d	Si bd	P abcd	S abcd	Cl abcd	Ar a
K a	Ca	Sc	Ti d	V d	Cr d*	Mn c*	Fe d	Co	Ni	Cu	Zn	Ga bd	Ge bd	As abcd	Se bcd	Br abd	Kr ad
Rb a	Sr d	Y	Zr d	Nb d	Mo d	Tc cd	Ru cd	Rh a	Pd	Ag a	Cd a	In a	Sm bd	Sb bd	Te bcd	I abd	Xe ad
Cs a	Ba a	La*	Hf d	Hf d	W d	Re cd	Os cd	Ir d	Pt	Au a	Hg ad	Tl a	Pb	Bi ab	Po ad	At ab	Rn ad
Fr a	Ra	Ac**															
			Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th**	Pa d	U d	Np d	Am	Cm	Bk	Cf	Es	Fm	Mv	No			

Key to volatile form of element: a - Element; b - Hydride; c - Oxide; c* - Permanganic acid; c$^+$ - Boric acid; d - Halides; d* - Chromyl chloride

(From Coomber, 1975)

McMillan (1975) states:

> "While many of the volatile species are commonly encountered and a large proportion can be produced from aqueous solutions, a significant number are rarely met. The volatilization of highly reactive materials and those with high boiling points are only used in special circumstances, e.g., for very rapid separations. ... Many other volatile compounds have been used to separate the elements, including sulphides, carbonyls, stable organic complexes ... , and fluorinated β-diketones for the lanthanides.
>
> "Separation ... is achieved by differentiation during the volatilization process, fractionation by transfer, and selective collection. Gaseous evolution can be controlled by making use of differences in vapor pressure with temperature, adjustment of the oxidation state of the element in solution or by alteration of the matrix, in order to change the chemical combination of the element. Once gaseous, additional separation is possible and physical processes can be adopted such as gas chromatography, zone refining, fractional distillation, electrostatic precipitation, filtration of condensed phases and low temperature trapping. Chemical methods used are mainly based on the selective trapping of interfering substances by solid or liquid reagents. The methods of preferential collection of the species sought are similar to those used in the transfer stage."

Both solid and liquid samples can be used in volatilization separations (Krivan, 1986):

> "With solid samples, there are several types of separation methods. The most important of them are ones in which (1) the gas forms a volatile compound with only the trace elements and not the matrix, (2) the gas forms a volatile compound with the matrix but not the trace elements, and (3) volatile compounds are formed with both the matrix and the trace elements. Different gases have been used in separation by volatilization, including inert gases N_2, He, and Ar and the reactive gases H_2O, O_2, H_2, ... F_2, and HF. The apparatus usually consists of three parts: gas regulation and purification, oven with temperature programming and control, and condensation or adsorption with temperature regulation.
>
> "The radiotracer technique provides the best way to determine the recoveries of trace elements in the volatilization process and to optimize the separation with respect to the pertinent experimental parameters."

14.5.3 Distillation Principles

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

Distillation has been widely used for separating organic mixtures but this approach has less applicability in inorganic analysis (Korkisch, 1969). Korkisch (1969) states: "Nevertheless, some of the elements of interest to radiochemists can be very effectively separated by distillation as their volatile chlorides, bromides, and oxides .... [T]hese elements are germanium (Ge), selenium (Se), technetium (Tc), rhenium (Re), ruthenium (Ru), and osmium (Os)." (Also see DOE, 1997, Method RP530). Two common analytes determined through distillation, tritium and ^{226}Ra, by radon emanation are discussed below.

Specific distillation principles are commonly found in chemistry reference and textbooks. For a theoretical discussion of distillation see Peters (1974) and Perry and Weisberger (1965). Distillation procedures are discussed for many inorganic applications in Dean (1995) and for less common radioanalytes in DeVoe (1962) and Kuska and Meinke (1961).

14.5.4 Separations in Radiochemical Analysis

The best known use of distillation in radiochemical analysis is in the determination of tritium (EPA, 1984; DOE, 1997). Water is the carrier as simple distillation is used to separate tritium from water or soil samples. For determination of tritium, the aqueous sample is treated with a small amount of sodium hydroxide (NaOH) and potassium permanganate ($KMnO_4$), and it is then distilled. The early distillate is discarded, and a portion of the distillate is collected for tritium determination by liquid scintillation counting. The alkaline treatment prevents other radionuclides, such as radioiodine or radiocarbon, from distilling over with the tritium (^{3}H), and the permanganate (MnO_4^{-1}) treatment destroys trace organic material in the sample that could cause quenching during the counting procedure.

Larger samples are distilled using a round-bottom flask, while a MICRO DIST® tube can be used for smaller samples (DOE, 1997, Method RP580). The distillate can be added directly to a liquid scintillation cocktail (EPA, 1980, Method 906.0), or further enriched by acid electrolysis (DOE, 1990 and 1997, Method ^{3}H-01) or alkaline electrolysis (DOE, 1990 and 1997, Method ^{3}H-02).

Iodine is separated from aqueous samples by distillation from acidic solutions into alkaline solutions (EPA, 1973). Iodide (I^{-1}) is added as carrier; but nitric acid (HNO_3) as part of the acid solution, oxidizes the anion to molecular iodine as the mixture is heated for distillation.

One determination of ^{79}Se employs an optional purification step, distillation of the metal as selenous acid, H_2SeO_3 (DOE, 1997, Method RP530). The solution is maintained with excess bromine (Br_2) and hydrobromic acid (HBr) to hold the selenium in the oxyacid form during the distillation. Technetium can be separated from other elements, or can be separated from ruthenium, osmium, or rhenium by distillation of their oxides (Friedlander et al., 1981). Metals are sometimes distilled in their elemental form—polonium in bismuth or lead (McMillan, 1975).

Radium-226 in solution can be determined by de-emanating its gaseous progeny ^{222}Rn into an ionization chamber or scintillation cell. Generally, the procedure initially involves the concentration of radium by coprecipitation with barium sulfate ($BaSO_4$). The barium sulfate is then dissolved in an EDTA solution, transferred to a sealed bubbler, and stored to allow for the ingrowth of ^{222}Rn. Following sufficient in-growth, the ^{222}Rn is de-emanated by purging the solution with an inert gas, such as helium (He) or argon (Ar), and is transferred via a drying tube to a scintillation cell or ionization chamber. After the short-lived ^{222}Rn progeny have reached secular equilibrium with the ^{222}Rn (approximately four hours), the sample is counted to determine alpha activity (EPA, 1980, Method 903.1; DOE, 1990 and 1997, Methods Ra-01 through Ra-07; Sedlet, 1966; Lucas, 1990).

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

14.5.5 Advantages and Disadvantages of Volatilization

14.5.5.1 Advantages

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

14.5.5.2 Disadvantages

- Relatively few volatile elements or inorganic compounds are available.
- Atmosphere can alter the nature of a volatile form of the tracer or surface material.

- Effects of experimental parameters (carrier gas, gas flow, temperature, time, and recovery) are highly variable.
- Precautions are sometimes necessary to avoid loss of volatile radionuclide substances during subsequent procedures.
- Some systems require high-temperature, complex equipment.
- Contamination of distillate by carrier, spray, or mechanical entrapment is a potential problem.

14.6 Electrodeposition

14.6.1 Electrodeposition Principles

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

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

$$E=E^0 - RT/nF \ln(a_p/a_r)$$

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

$$E=E^0 - RT/nF \ln(\gamma_p c_p/\gamma_r c_r)$$

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

$$E = E^0 - RT/nF \ln(c_p/c_r)$$

At concentrations less than 10^{-6} M, electrodeposition may show considerable deviations from behavior of macroamounts of elements whose behavior partly depends on the nature and previous treatment of the electrode (Adolff and Guillaumont, 1993). Inconsistent behavior is the result of heterogeneity of the surface metal, a very important consideration when electrodepositing radionuclides at very low concentrations. The spontaneity predicted by the Nernst equation for macroconcentrations of ions in solution at controlled potential is not always observed for microconcentrations (Choppin et al., 1995). The activity of radionuclide ions is usually unknown at low concentrations even if the concentration is known, because the activity coefficient (γ) is dependent on the behavior of the mixed electrolytic system. In addition, the concentration might not be accurately known because ions might adsorb on various surfaces, form complexes with impurities, or precipitate on the electrode, for example. (See Section 14.9.3.7, "Oxidation and Reduction," for another application of the Nernst equation.) Separation is limited partly because electrodeposition from very dilute solutions is slow, but it is also limited because it rarely leads to complete separation of one element from many others (Coomber, 1975). Overall, the behavior of an element during an electrochemical process is determined by its electrochemical potential, which depends on the nature of the ion; its chemical form, its concentration, the general composition of the electrolyte, the current density, material and design of the electrode, and construction features of the electrochemical cell (Zolotov, 1990).

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

14.6.2 Separation of Radionuclides

Although electrodeposition is not frequently used as a radiochemical separation technique, several radionuclides [including iron (Hahn, 1945), cadmium (Wright, 1947), and technetium (Flagg, 1945)] have been isolated by electrodeposition on a metal electrode. Electrodeposition is, however, the standard separation technique for polonium, copper, and platinum. Polonium is isolated through deposition on nickel from a strong hydrochloric acid (DOE, 1990 and 1997, Method Po-01). This separation is very specific, and, therefore, can be accomplished in the presence of many other radionuclides. Electrodeposition at a mercury cathode has also been used to separate technetium from fission products and for group separation of fission products (Coomber, 1975). Numerous metals have been deposited on thin metal films by electrolysis with a magnesium cathode. According to Coomber, "Electrodeposition of metals can be sensitive to the presence of other substances" (Coomber, 1975). Deposition of polonium on silver is inhibited by iron unless a reducing agent is present; and the presence of fluoride (F^{-1}), trace amounts of rare earths, can inhibit the deposition of americium. "In many cases the uncertainties of yield can be corrected by the use of another radioisotope as an internal standard" (Coomber, 1975).

14.6.3 Preparation of Counting Sources

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

Sill and Williams (1981) and Hindman (1983, 1986) contend that coprecipitation is the preferred method for preparation of sources for alpha spectrometry and that it should be assessed when electrodeposition is being considered. Also see Section 14.8.4, "Coprecipitation."

14.6.4 Advantages and Disadvantages of Electrodeposition

14.6.4.1 Advantages

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

14.6.4.2 Disadvantages

- Not applicable to many radionuclides.
- Sensitive to the presence of other substances.
- For tracer-level quantities, the process is relatively slow, it seldom leads to complete separation of one element from many others, and there is usually no direct comparison of concentration in solution to deposited activity.
- Takes longer than microprecipitation, because it requires evaporation of solutions after column separation and ashing to remove all organic residue.

- Subject to interference from such metals as Fe or Ti.
- Subject to interference from such ions as fluoride.

14.7 Chromatography

14.7.1 Chromatographic Principles

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

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

The most common phase pairs used in chromatography are a mobile liquid phase in contact with a solid phase. The liquid phase can be a pure liquid, such as water or an organic solvent, or it can be a solution, such as methyl alcohol, sodium chloride in water, or hexane in toluene. The solid phase can be a continuous material such as paper, or a fine-grained solid such as silica, powdered charcoal, or alumina. The fine-grained solid can also be applied to a supporting material, such as paper, plastic, or glass, to form a coat of continuous material. Alternatively, gas/liquid phase systems can consist of an inert gas, such as nitrogen or helium, in conjunction with a high-boiling point liquid polymer coated on the surface of a fine-grained inert material, such as firebrick. This system is called gas-liquid phase chromatography (GLPC), or simply gas chromatography (GC). In each system, both phases play a role in the separation by offering a physical or chemical characteristic that will result in differential distribution of the components of the analytical mixture being separated. Liquid-liquid phase systems are similar to gas/liquid phase systems in that one of the liquid phases is bound to an inert surface and remains stationary. These systems are often referred to as liquid-partition chromatography or liquid-phase chromatography (LPC), because they are essentially liquid-liquid extraction systems with one mobile and one immobile phase (Section 14.4, "Solvent Extraction").

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

14.7.2 Gas-Liquid and Liquid-Liquid Phase Chromatography

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

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

14.7.3 Adsorption Chromatography

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

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

14.7.4 Ion-Exchange Chromatography

14.7.4.1 Principles of Ion Exchange

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

Ion-exchange methods are based on the reversible exchange of metal ions between a liquid phase, typically water, and a solid ionic phase of opposite charge, the resin. The resin competes with the ion-solvent interactions in the liquid phase, primarily ion-dipole interactions and hydrogen bonding, to produce the selective partition of ions, causing separation. The solid phase consists of an insoluble, but permeable, inert polymeric matrix that contains fixed charged groups (exchange sites) associated with mobile counter-ions of opposite charge. It is these counter-ions that are exchanged for other ions in the liquid phase. Resins are either naturally occurring substances, such as zeolites (inorganic silicate polymers) or synthetic polymers. The synthetic resins are organic polymers with groups containing the exchange sites. The exchange sites are acid or base groups (amines, phenols, and carboxylic or sulfonic acids) used over a specific pH range where they are in their ionic form. Typical exchange groups for cations (K^{+1}, Ca^{+2}, and UO_2^{+2}) are the sulfonate anion, RSO_3^{-1}, or the carboxylate anion, $RCOO^{-1}$. The quaternary-amine cation, RNH_3^{+1}, or its derivative, is a common exchange group for anions (Cl^{-1}, OH^{-1}, and $UO_2(SO_4)_3^{-4}$).

In a practical description of ion-exchange equilibria, the weight distribution coefficient, K_d, and the separation factor, α, are significant. The weight distribution coefficient is defined as:

$$K_d = \frac{[C_1 / g_{resin}]}{[C_2 / mL_{solution}]}$$

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

$$\text{Separation factor } (\alpha) = \frac{[K_{d,a}]}{[K_{d,b}]}$$

where *a* and *b* refer to a pair of ions. This ratio determines the separability of the two ions; separation will only be achieved if α ≠ 1. The more that α deviates from unity, the easier it will be to obtain separation.

An example of the separation process is the cation-exchange resin. It is usually prepared for separation procedures as a hydrogen salt of the exchange group. Separation occurs when an aqueous solution of other cation (e.g., Na^{+1}, Ca^{+2}, Al^{+3}, or Cs^{+1}) comes in contact with the resin. . Different ions bond selectively to the exchange group, depending on the separation conditions, displacing the counter-ion that is present in the prepared resin as follows:

$$R_{esin}SO_3^{-1}\,H^{+1} + Cs^{+1} \rightarrow R_{esin}SO_3^{-1}Cs^{+1} + H^{+1}$$

Diffusion is an important process during ion exchange; the solute ions must penetrate the pores of the spherical resin beads to exchange with the existing ions. Equilibrium is established between each ion in the analyte solution and the exchange site on the resin. The ion least tightly bonded to the exchange site and most solvated in solution spends more time in solution. Selective bonding is a factor of the size and charge of the ion, the nature of the exchange group, and the pH and ionic strength of the media. The order of strength of bonding at low acid concentrations for group 1 cations is H^{+1} or $Li^{+1} < Na^{+1} < K^{+1} < Rb^{+1} < Cs^{+1}$ (Showsmith, 1984). Under the appropriate conditions, for example, Cs^{+1} will bond exclusively, or Cs^{+1} and Rb^{+1} will bond, leaving the remaining cations in solution. The process can be operated as a batch operation or via continuous-flow with the resin in an ion-exchange column. In either case, actual separation is achieved as the equilibrated solution elutes from the resin, leaving select ions bonded to the resin and others in solution. The ion that spends more time in solution elutes first. The ability to "hold" ionic material is the resin capacity, measured in units of mg or meq per gram of resin. Eventually, most of the exchange groups are occupied by select ions. The resin is essentially saturated, and additional cations cannot bond. In a continuous-flow process, breakthrough will then occur. At this time, added quantities of select cations (Cs^{+1} or Cs^{+1} and Rb^{+1} in this example) will pass through the ion-exchange column and appear in the output solution (eluate). No further separation can occur after breakthrough, and the bonded ions must be remove to prepare the column for additional separation. The number of bed volumes of incoming solution (eluant) that passes through a column resin before breakthrough occurs provides one relative measure of the treatment capacity of the resin under the conditions of column use. The bonded cations are displaced by adjusting the pH of the medium to change the net charge on the exchange groups. This change alters the ability of the exchange groups to attract ions, thereby replacing the bonded cations with cations that bond more strongly. More commonly, the resin is treated with a more concentrated solution of the counter-ion—H^{+1} in this example. Excess H^{+1} favors the equilibrium that produces the initial counter-ion form of the exchange group. This process that returns the column to its original form is referred to as “regeneration.”

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

- In dilute solutions, the stationary phase will show preference for ions of higher charge.
- The selectivity of ion exchangers for ions increases with the increase of atomic number within the same periodic group, i.e., $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.
- The higher the polarizability and the lower the degree of solvation (favored by low charge and large size), the more strongly an ion will be adsorbed.
- Resins containing weakly acidic and weakly basic groups are highly selective towards H^+ and OH^- ions. Ion-exchange resins that contain groups capable of complex formation with particular ions will be more selective towards those ions.
- As cross-linking is increased (see discussion of resins below), resins become more selective in their behavior towards ions of different sizes.
- No variation in the eluent concentration will improve the separation for ions of the same charge; however, for ions of different net charges, the separation does depend on the eluent concentration.

14.7.4.2 Resins

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

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

14.7.7, "Chromatographic Methods").

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

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

- Resins should not be allowed to dry out, especially during analysis. Rehydration of dried resins will result in cracking; these resins should not be used.
- Nonionic and weakly ionic solutes may be absorbed (not exchanged) by the resin. These materials, if present during analysis, can alter the exchange characteristics of the resin for certain ions.
- Particulate matter present in the analyte solution may be filtered by the resin. This material will have several undesired effects, such as decreased flow rate, reduced capacity, and ineffective separation.
- Organic solvents suspended in the analyte solution from previous separation steps can be adsorbed by the resin creating separation problems.

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

TABLE 14.8 — Typical functional groups of ion-exchange resins

Cation Exchangers	Anion Exchangers
$-SO_3H$	$-NH_2$
- COOH	- NHR
- OH	$-NR_2$
- SH	$-NR_3^+$

R=alkyl group

The sulfonate resins are known as strong acid cation (SAC) resins because the anion is derived from a strong sulfonic acid (RSO_3H). Likewise, the carboxylate resins are known as weak acid cation (WAC) resins because the anion is derived from a weak carboxylic acid (RCOOH). R in the formulas represents the inert matrix. The quaternary-amine cation (RNH_3^{+1}) or its derivatives, represents the common exchange group for anions. Other functional groups can be used for specific purposes.

Several examples from the literature illustrate the use of ion-exchange chromatography for the separation of radionuclides. Radium is separated from other alkaline-earth cations (Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, and Ba^{+2}) in hydrochloric solutions on sulfonated polystyrene resins (Kirby and Salutsky, 1964), or converted to an anionic complex with citrate or EDTA and separated on a quaternary ammonium polystyrene resin (Sedlet, 1966).

Anion-exchange resins separate anions by an analogous process beginning with a prepared resin, usually in the chloride form ($RNH_3^{+1}Cl^{-1}$), and adding a solution of ions. Anion-exchange chromatography is used in one step of a procedure to isolate thorium for radioanalysis by alpha counting (EPA, 1984). Thorium cations (Th^{+4}) form anionic nitrate complexes that bind to an anion-exchange resin containing the quaternary complex, $R\text{-}CH_2\text{-}N(CH_3)_3^{+1}$. Most metal ion impurities do not form the complex and, as cations, they do not bind to the exchanger, but remain with the liquid phase. Once the impurities are removed, thorium itself is separated from the resin by treatment with hydrochloric acid (HCl) that destroys the nitrate complex, leaving thorium in its +4 state, which will not bind to the anionic exchanger. A selection of commercially available resins commonly employed in the radiochemistry laboratory is given in Table 14.9.

TABLE 14.9 — Common ion-exchange resins (*)

Resin type & nominal % cross-link	Minimum wet capacity meq • mL^{-1}	Density (nominal) g • mL^{-1}	Description
Anion-exchange resins — gel type — strongly basic — quaternary ammonium functionality			
Dowex™, AG™ or Eichrom™ 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.
Dowex, AG or Eichrom 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.
Anion-exchange resins — gel type — intermediate basicity			
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.
Anion-exchange resins — gel type — weakly basic — polyamine functionality			
Dowex or AG 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.
Amberlite™ IRA-68	1.6	1.06	Acrylic-DVB with unusually high capacity for large organic molecules.
Cation-exchange resins - gel type - strongly acidic - sulfonic acid functionality			

Resin type & nominal % cross-link	Minimum wet capacity meq • mL^{-1}	Density (nominal) g • mL^{-1}	Description
Dowex, AG or Eichrom 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.
Dowex, AG or Eichrom 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.
Amberlite IR-120	1.9	1.26	8% styrene-DVB type; high physical stability.
Selective ion-exchange resins			
Duolite™ GT-73	1.3	1.30	Removal of Ag, Cd, Cu, Hg, and Pb.
Amberlite IRA-743A	0.6	1.05	Boron-specific.
Amberlite IRC-718	1.0	1.14	Removal of transition metals.
Chelex® 100	0.4	0.65	Weakly acidic chelating resin with S-DVB matrix for heavy metal concentration.
Eichrom Diphonix®			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.
Anion exchanger — macroreticular type — strongly basic — quaternary ammonium functionality			
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.
Cation-exchange resin — macroreticular type — sulfonic acid functionality			
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.
Microcrystalline exchanger			
AMP-1	4.0		Microcrystalline ammonium molybophosphate with cation exchange capacity of 1.2 meq/g. Selectively exchanges larger alkali-metal ions from smaller alkali-metal ions, particularly cesium.

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

The behavior of the elements on anion- and cation-exchange resins is summarized for several resins in Faris and Buchanan (1964), Kraus and Nelson (1956), and Nelson et al. (1964). The behavior in concentrated HCl is illustrated for cations on cation-exchange resins in Figure 14.3 (Dorfner, 1972) and for anions on anion-exchange resins in Figure 14.4 (Dorfner, 1972).

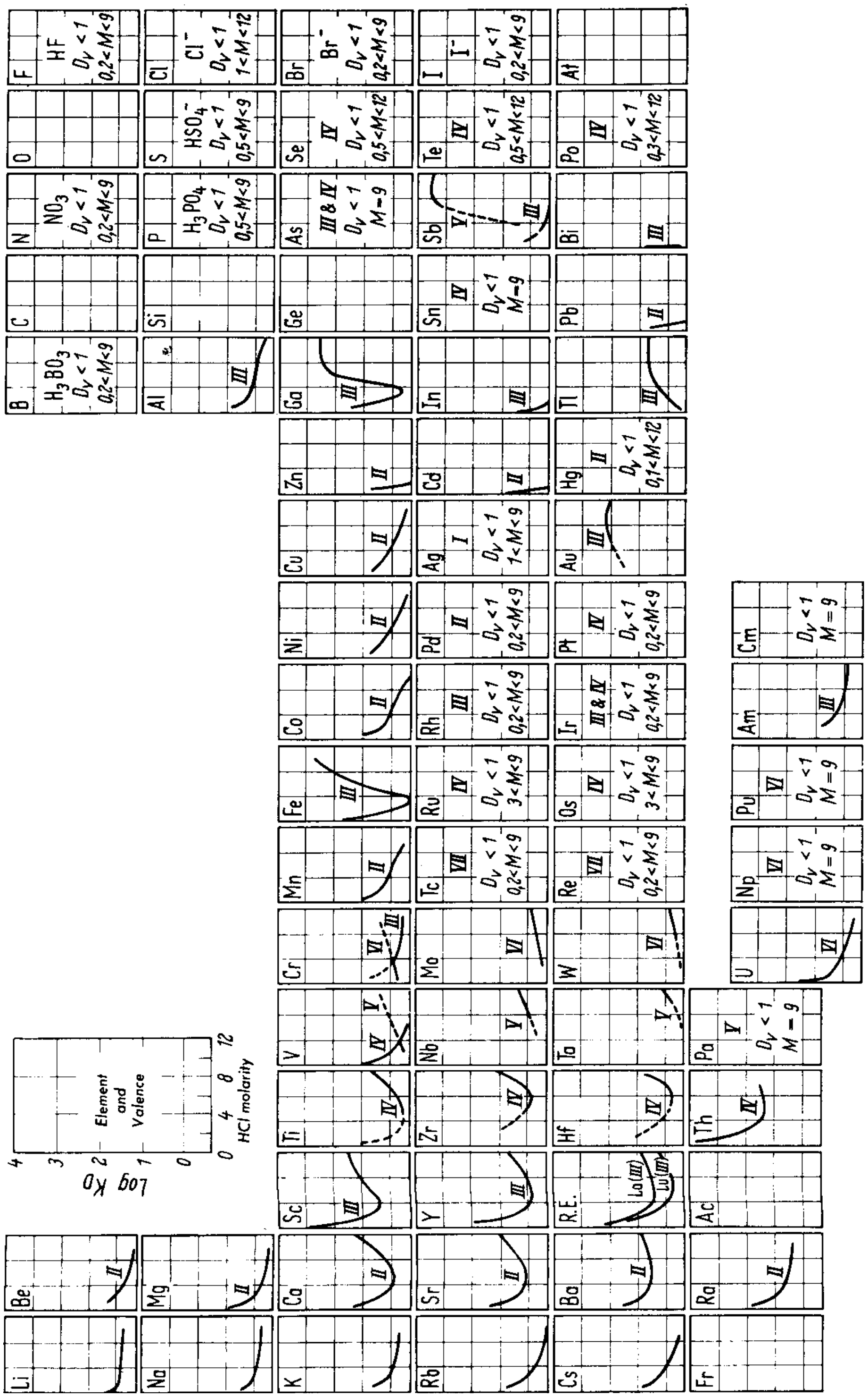


FIGURE 14.3 — The behavior of elements in concentrated hydrochloric acid on cation-exchange resins

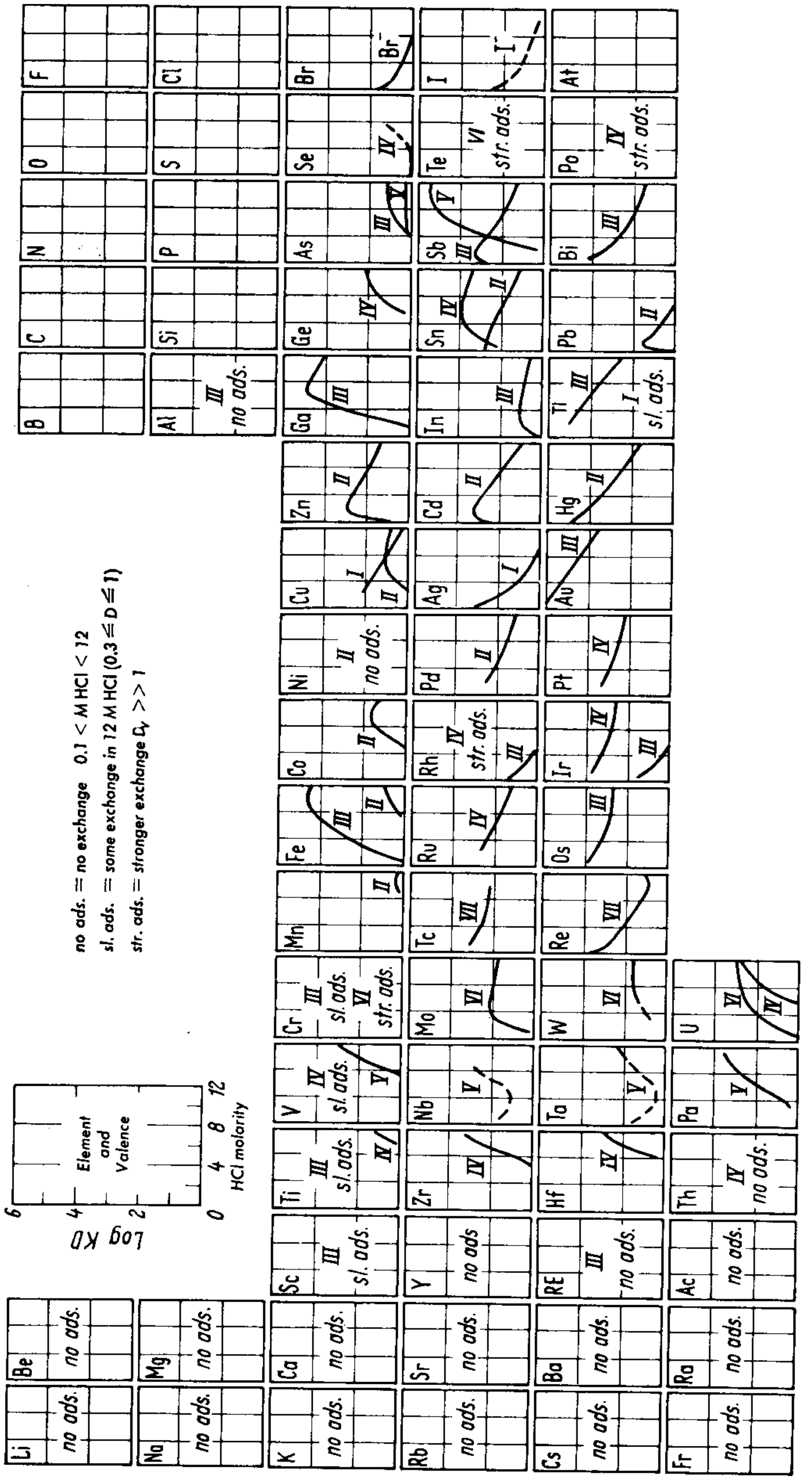


Figure 14.4 —The behavior of elements in concentrated hydrochloric acid on anion-exchange resins

14.7.5 Affinity Chromatography

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

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

14.7.6 Gel-Filtration Chromatography

Another physical property that is used to separate molecules by a chromatographic procedure is the effective size (molecular weight) of the molecule. High molecular-weight ions can also be separated by this procedure. The method is known by several names, including gel-filtration chromatography, molecular-sieve filtration, exclusion chromatography, and gel-permeation chromatography. This technique is primarily limited to substances such as biomolecules with molecular weights greater than 10,000 daltons (1.657×10^{-20} g). In similar types of solutions (similar solutes and similar concentrations), the molecules or ions have a similar shape and molecular weight that is approximately proportional to the hydrodynamic diameter (size) of the molecule or ion. The solid phase consists of a small-grain inert resin that contains microscopic pores in its matrix that will allow molecules and ions up to a certain diameter, called included particles, to enter the resin. Larger particles are excluded. Of the included particles, the smaller ones spend more time in the matrices. Separation of the molecules or ions is based on the fact that those substances that are excluded are separated in a batch from the included substances, while those that are included are separated by size. The log of the molecular weight of the included molecules or ions is approximately inversely proportional to the time the particles spend in the matrix.

14.7.7 Chromatographic Laboratory Methods

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

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

Metal columns can withstand considerably more pressure than glass columns. High-pressure liquid chromatography (HPLC) employs stainless steel columns and solid phases designed to withstand high pressures without collapsing. The method is noted for its rapid separation times because of relatively high flow rates under high pressures (up to almost 14 MPa). For this reason, the acronym HPLC alternatively represents high-performance liquid chromatography. HPLC is often performed with a liquid-partition technique between an aqueous phase and organic phase, but gel filtration, ion exchange, and adsorption methods are also employed. In the case of liquid-partition separations, either a stationary aqueous phase or stationary organic phase is selected. The former system is referred to as normal phase chromatography and the latter as reversed phase chromatography, a holdover from the first applications of the technique that employed a stationary aqueous phase. The aqueous phase is made stationary by adsorption onto a solid support, commonly silica gel, cellulose powder, or polyacrylamide. An organic stationary phase is made from particles of a polymer such as polyvinyl chloride or Teflon™. Reversed phase HPLC has been used to separate individual elements of the lanthanides and actinides and macroquantities of actinides (Choppin et al., 1995).

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

14.7.8 Advantages and Disadvantages of Chromatographic Systems

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

14.7.8.1 Advantages

- Highly selective.
- Highly efficient as a preconcentration method.
- Works as well with carrier-free tracer quantities as with weighable amounts.
- Produces a high yield (recovery).
- Can separate radionuclides from interfering counter-ions.
- Simple process requiring simple equipment.
- Wide scope of applications.
- Can handle high volumes of sample.

14.7.8.2 Disadvantages

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

14.8 Precipitation and Coprecipitation

14.8.1 Introduction

Two of the most common and oldest methods for the separation and purification of ions in radioanalytical chemistry are precipitation and coprecipitation. Precipitation is used to isolate and collect a specific radionuclide from other (foreign) ions in solution by forming an insoluble compound. Either the radionuclide is precipitated from solution itself, or the foreign ions are precipitated, leaving the radionuclide in solution. Sometimes a radionuclide is present in solution at sub-micro concentrations, i.e., levels so low that the radionuclide will not form an insoluble compound upon addition of a counter-ion. In these cases, the radionuclide can often be brought down from solution by coprecipitation, associating it with an insoluble substance that precipitates from solution. This phenomenon is especially important in gravimetric analysis and radiochemistry. In gravimetric analysis, carrying down of impurities is a problem. For radiochemists, coprecipitation is a valuable tool.

14.8.2 Solutions

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

- Solubility is defined as the concentration of solute in solution that exists in equilibrium with an excess of solute; it represents the maximum amount of solute that can dissolve in a given amount of the solvent. The general solubilities of many of the major compounds of concern are described in Table 14.10.

- An unsaturated solution is one in which the concentration of the solute is less than the solubility. When additional solute is added to an unsaturated solution, it dissolves.

- A saturated solution is one that is in equilibrium with an excess of the solute. The concentration of a saturated solution is equal to the solubility of the solute. When solute is added to the saturated solution, no more solute dissolves.

- A supersaturated solution is a solution in which the concentration of solute is temporarily greater than its solubility—an unstable condition. Therefore, when additional solute is added to a supersaturated solution, solute comes out of solution as solid until the concentration decreases to that of the saturated solution.

TABLE 14.10 — General solubility behavior of some cations of interest (1)

The Common Cations

Na^{+1}, K^{+1}, NH_4^{+1}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Al^{+3}, Cr^{+3}, Mn^{+2}, Fe^{+2}, Fe^{+3},
Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Ag^{+1}, Cd^{+2}, Sn^{+2}, Hg_2^{+2}, Hg^{+2}, and Pb^{+2}

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

Under the class of *mainly soluble substances*:

- All nitrates (NO_3^-) are soluble.
- All acetates ($C_2H_3O_2^-$) are soluble.
- All chlorides (Cl^-), bromides (Br^-), and iodides (I^-) are soluble, except for those of silver, mercury, and lead. $PbCl_2$ and $PbBr_2$ are sparingly soluble in cold water, and more soluble in hot water.
- All sulfates (SO_4^{-2}) are soluble, except those of barium, strontium, and lead. $CaSO_4$, Ag_2SO_4, and Hg_2SO_4 are sparingly soluble.
- Most salts of sodium (Na), potassium (K), and ammonium (NH4+) are soluble. Notable exceptions are $NaSb(OH)_6$, $K_3Co(NO_2)_6$, K_2PtCl_6, $(NH_4)_2PtCL_6$, and $(NH_4)_3Co(NO_2)_6$.

Under the class of *mainly insoluble substances*:

- All hydroxides (OH^{-1}) are insoluble, except those of the alkali metals (Li, Na, K, Rb, and Cs), ammonium, and barium (Ba). $Ca(OH)_2$ and $Sr(OH)_2$ are sparingly soluble.

- All normal carbonates (CO_3^{-2}) and phosphates (PO_4^{-3}) are insoluble, except those of the alkali metals and ammonium. Many hydrogen carbonates and phosphates are soluble, i.e., $Ca(HCO_3)_2$, $Ca(H_2PO_4)_2$.

- All sulfides (S^{-2}), except those of the alkali metals, ammonium, and the alkaline-earth metals (Be, Mg, Ca, Sr, Ba, and Ra), are insoluble. Both aluminum- and chromium sulfide are hydrolyzed by water, resulting in the precipitation of $Al(OH)_3$ and $Cr(OH)_3$.

- Some cations, such as Ba^{+2}, Pb^{+2}, and Ag^{+1}, form insoluble chromates (CrO_4^{-2}), which can be used as a basis for separation.

Actinide Elements

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

- The *fluorides (F^-), oxalates ($C_2O_4^{-2}$), hydroxides (OH^-), and phosphates* are insoluble.
- The *nitrates, halides (except fluorides), sulfates, perchlorates (ClO_4^-), and sulfides* are all soluble.

(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.

14.8.3 Precipitation

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).

A precipitation process should satisfy three main requirements:

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

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.

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

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

Solubility equilibrium refers to the equilibrium that describes a solid (s) dissolving in solution (soln), such as strontium carbonate dissolving in water, for example:

$$SrCO_3(s) \rightleftharpoons Sr^{+2}\,(soln) + CO_3^{-2}\,(soln)$$

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

$$Sr^{+2}\,(soln) + CO_3^{-2}\,(soln) \rightarrow SrCO_3\!\downarrow\,(s)$$

The solubility product constant, K_{sp}, is the equilibrium constant for the former process, a solid dissolving and forming ions in solution. Leussing (1959) explains K_{sp} in general terms:

> "For an electrolyte, M_mN_n, which dissolves and dissociates according to the equation:
>
> $$M_mN_n(s) \rightleftharpoons M_mN_n(soln) \rightleftharpoons mM^{+n}(soln.) + nN^{-m}(soln)$$
>
> "The equilibrium conditions exists that:
>
> $$a_{MmNn(s)} = a_{MmNn(soln)} = a^{m}_{M+n(soln)} \cdot a^{n}_{N-m(soln.)}$$
>
> "[The value *a* is the *activity* of the ions in solution, a measure of the molar concentration (moles/L) of an ion in solution under ideal conditions of infinite dilution.] (Also see Section 14.6.1, "Principles of Electrodeposition," for a discussion of activity as applied to the Nernst equation.) [This equation] results in the familiar solubility product expression since the activity of a solid under given conditions is a constant. Expressing the activities in terms of the product of molar concentrations and activity coefficients, γ [a measure of the extent the ion deviates from ideal behavior in solution; thus $a = \gamma \cdot c$ where $\gamma \leq 1$], [this] equation becomes...
>
> $$[M^{+n}]^m\,[N^{-m}]^n\,\gamma^{m}_{M+n}\,\gamma^{n}_{N-m} = \text{a constant} = K_{sp}\text{ ''}$$

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

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

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

$$K_{sp} = [Sr^{+2}][CO_3^{-2}] = 1.6\times10^{-9}$$

In order for the carbonate to precipitate, the product of the concentration of the ions in solution representing the ions in the equilibrium expression, the common ions, must exceed the value of the K_{sp}. The concentration of each common ion does not have to be equal. For example, if $[Sr^{+2}]$ is 1×10^{-6} molar, then the carbonate ion concentration must be greater than 0.0016 molar for precipitation to occur because $(1\times10^{-6}) \times (0.0016) = 1.6\times10^{-9}$.

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

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

> “If a chemist mixes 100 mL of 0.0050 M NaCl with 200 mL of 0.020 M $Pb(NO_3)_2$, will lead chloride precipitate? The ion product, *Q*, must be calculated and compared to K_{sp} for the process:
>
> $$PbCl_2(s) \rightleftharpoons Pb^{+2}(soln) + 2\ Cl^{-}(soln)$$
>
> “After the two solutions are mixed, $[Pb^{+2}] = 1.3\times10^{-2}$ M ($0.2\ L \times 2.0\times10^{-2}$ M/0.3 L), and $[Cl^{-}] = 1.7\times10^{-3}$ M ($0.1\ L \times 5.0\times10^{-3}$ M/0.3 L). The value for the ion product is calculated from the expression
>
> $$Q = [Pb^{+2}]\ [Cl^{-}]^2 \text{ or } [1.3\times10^{-2}]\ [1.7\times10^{-3}]^2$$
>
> $$Q = 3.8\times10^{-8}$$
>
> “The numerical value for K_{sp} is 1.6×10^{-5}. Because the ion product Q is less than K_{sp}, no precipitate will form. Only when the ion product is greater than K_{sp} will a precipitate form.”

Conditions in the solution phase can affect solubility. For example, the solubility of an ion is lower in an aqueous solution containing a common ion, one of the ions comprising the compound, than in pure water because a precipitate will form if the K_{sp} is exceeded. This phenomenon is known as the common ion effect and is consistent with LeChatelier’s Principle. For example, the presence of soluble sodium carbonate (Na_2CO_3) in solution with strontium ions can cause the precipitation of strontium carbonate, because carbonate ions from the sodium salt contribute to their overall concentration in solution and tend to reverse the solubility equilibrium of the “insoluble” strontium carbonate:

$$Na_2CO_3(s) \rightleftharpoons 2\ Na^{+1}(soln) + CO_3^{-2}(soln)$$

$$SrCO_3(s) \rightleftharpoons Sr^{+2}(soln) + CO_3^{-2}(soln)$$

Alternatively, if a complexing agent or ligand is available that can react with the cation of a precipitate, the solubility of the compound can be markedly enhanced. An example from Section 14.3.4.3, "Formation and Dissolution of Precipitates," provides an illustration of this phenomenon. In the determination of ^{90}Sr, Sr^{+2} is separated from the bulk of the solution by direct precipitation of the sulfate ($SrSO_4$). The precipitate is redissolved by forming a complex ion with EDTA, $Sr(EDTA)^{-2}$, to separate it from lanthanides and actinides (DOE, 1997, Method RP520):

$$SrSO_4(s) \rightarrow Sr^{+2}(soln) + SO_4^{-2}(soln)$$

$$Sr^{+2}(soln) + EDTA^{-4} \rightarrow Sr(EDTA)^{-2}(soln)$$

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

$$Fe^{+3} + H_2O \rightarrow Fe(OH)^{+2} + H^{+1}$$

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

- Polymorphism is the existence of a chemical substance in two or more crystalline forms. For example, calcium carbonate can have several different forms; only one form of a crystal is stable at a given temperature. At ordinary pressures and temperatures, calcite with a solubility of 0.028 g/L, is the stable form. Aragonite, another common form of calcium carbonate ($CaCO_3$), has a solubility of 0.041g/L at these conditions. It is not necessarily calcite that precipitates when solutions of sodium carbonate and calcium nitrate are mixed. Extremely low concentrations of large cations, such as strontium, barium, or lead, promote the precipitation of aragonite over calcite (Wray and Daniels, 1957). On aging, the more soluble aragonite converts to calcite.

- Various possible hydrates of a solid have different solubilities. For instance, at 25 °C, the molar solubility of gypsum ($CaSO_4 \cdot 2H_2O$) is 0.206 and that of anhydrite ($CaSO_4$) is 0.271.

- The solid phase can undergo a reaction with a salt in solution.

- Particle size of a solid can affect its solubility. It has been demonstrated that the solubility of smaller particles is greater than that of larger particles of the same material.

- Age of a precipitate can affect solubility. For example, Biederman and Schindler (1957) have demonstrated that the solubility of precipitated ferric hydroxide [$Fe(OH)_3$] undergoes a four-fold decrease to a steady state after 200 hours.

- Exchange of ions at the surface of the crystal with ions in the solution can affect the solubility of a solid. This effect is a function of the amount of surface available for exchange and is, therefore, greater for a finely divided solid. For example, Kolthoff and Sandell (1933) observed that calcium oxalate (CaC_2O_4) can exchange with either sulfate or barium ions:

$$CaC_2O_4(s) + SO_4^{-2}(soln) \rightarrow CaSO_4(s) + C_2O_4^{-2}(soln)$$

$$CaC_2O_4(s) + Ba^{+2}(soln) \rightarrow BaC_2O_4(s) + Ca^{+2}(soln)$$

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

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

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

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

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

14.8.3.2 Factors Affecting Precipitation

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

- *Rate of precipitation*. Formation of large, well-shaped crystals is encouraged through slow precipitation because fewer nuclei form and they have time to grow into larger crystals to the detriment of smaller crystals present. Solubility of the larger crystals is less than that of smaller crystals because smaller crystals expose more surface area to the solution. Larger crystals also provide less surface area for the absorption of foreign ions. Slow precipitation can be accomplished by adding a very dilute solution of the precipitant gradually, with stirring, to a medium in which the resulting precipitate initially has a moderate solubility.

- *Concentration of Ions and Solubility of Solids*. The rate of precipitation depends on the concentration of ions in solution and the solubility of the solids formed during the equilibrium process. A solution containing a low concentration of ions, but sufficient concentration to form a precipitate, will slow the process, resulting in larger crystal formation. At the same time, increasing the solubility of the solid, either by selecting the counter-ion for precipitation or by altering the precipitating conditions, will also slow precipitation. Many radionuclides form insoluble solids with a variety of ions, and the choice of precipitating agent will affect the solubility of the precipitate. For example, radium sulfate ($RaSO_4$) is the most insoluble radium compound known. Radium carbonate ($RaCO_3$) is also insoluble, but its K_{sp} is greater than that of radium sulfate (Kirby and Salutsky, 1964).

- *Temperature*. Precipitation at higher temperature slows nucleation and crystal growth because of the increased thermal motion of the particles in solution. Therefore, larger crystals form, reducing the amount of adsorption and occlusion. However, most solids are more soluble at elevated temperatures, effectively reducing precipitate yield; an optimum temperature balances these opposing factors.

- *Digestion.* Extremely small particles, with a radius on the order of one micron, are more soluble than larger particles because of their larger surface area compared to their volume (weight). Therefore, when a precipitate is heated over time (digestion) the small crystals dissolve and larger crystals grow ("Ostwald ripening"). Effectively, the small crystals are recrystallized, allowing the escape of impurities (occluded ions) and growth of larger crystals. This process reduces the surface area for adsorption of foreign ions and, at the same time, replaces the impurities with common ions that properly "fit" the crystal lattice. Recrystallization perfects the crystal lattice, producing a purer precipitate (see *Reprecipitation* on page 14-68). Digestion is used in an ^{131}I determination to increase the purity of the lead iodide (PbI_2) crystals (EPA, 1984).

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

- *Solvent*. The nature of the solvent affects the solubility of an ionic solid (precipitate) in the solvent. The polarity of water can be reduced by the addition of other miscible solvents such as alcohols, thereby reducing the solubility of precipitates. Strontium chromate ($SrCrO_4$) is soluble in water, but it is insoluble in a methyl alcohol (CH_3OH)-water mixture and can be effectively precipitated from the solution (Berg, 1963). In some procedures, precipitation is achieved by adding alcohol to an aqueous solution, but the dilution effect might reduce the yield because it lowers the concentration of ions in solution.

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

- *Stirring*. Stirring the solution during precipitation increases the motion of particles in solution and decreases the localized buildup of concentration of ions by keeping the solution thoroughly mixed. Both of these properties slow nucleation and crystal growth, thus promoting larger and purer crystals. This approach also promotes recrystallization because the smaller crystals, with their net larger surface area, are more soluble under these conditions. Virtually all radiochemical laboratories employ stirring with a magnetic stirrer during precipitation reactions.

- *Complex-Ion Formation*. Formation of complex ions can be used to hold back impurities from precipitating by producing a more soluble form of a solid. The classical example of this phenomenon is the precipitation of lead (Pb^{+2}) in the presence of silver ions (Ag^{+1}). Chloride ion (Cl^{-1}) is the precipitating agent that produces insoluble lead chloride ($PbCl_2$). In an excess of the agent, silver chloride (AgCl) is not formed because a soluble salt containing the complex ion, $AgCl_2^{-1}$ is formed. Complex-ion formation is also used to form precipitates (see Section 14.3, "Complexation").

- *pH Effect*. Altering the pH of aqueous solutions will alter the concentration of ions in the precipitation equilibrium by the common-ion effect, if the hydrogen ion (H^{+1}) or hydroxide ion (OH^{-1}) is common to the equilibrium. For example, calcium oxalate (CaC_2O_4) can be precipitated or dissolved, depending on the pH of the solution, as follows:

$$Ca^{+2} + C_2O_4^{-2} \rightarrow CaC_2O_4$$

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

$$H^{+1} + C_2O_4^{-2} \rightarrow HC_2O_4^{-1},$$

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

$$Sr^{+2} + CO_3^{-2} \rightarrow SrCO_3$$

$$H^{+1} + CO_3^{-2} \rightarrow HCO_3^{-1}$$

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

$$H_2S \rightarrow H^{+1} + HS^{-1}$$

$$HS^{-1} \rightarrow H^{+1} + S^{-2}$$

$$Pb^{+2} + S^{-2} \rightarrow PbS$$

The pH can also influence selective formation of precipitates. Barium chromate will precipitate in the presence of strontium at pH 4 to 8, leaving strontium in solution. Sodium carbonate is added and strontium precipitates after ammonia (NH_3) is added to make the solution more alkaline. This procedure is the basis for the separation of radium from strontium in the radioanalysis of strontium in drinking water (EPA, 1980).

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

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

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

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

$$CH_3CSNH_2 + 2\ H_2O \rightarrow CH_3COO^{-1} + H_2S + NH_4^{+1}$$

  Copper sulfide (CuS) coprecipitates technetium from a homogeneous medium by the generation of hydrogen sulfide by this method (EPA, 1973). Other agents alter the pH of the solution (see "*pH Effect*" on the previous page). Hydrolysis of urea, for example, produces ammonia, which raises the pH of a solution:

$$H_2NCONH_2 + H_2O \rightarrow CO_2 + 2\ NH_3$$

TABLE 14.11 — Summary of methods for utilizing precipitation from homogeneous solution

Precipitant	Reagent	Element Precipitated
Hydroxide	Urea	Al, Ga, Th, Fe^{+3}, Sn, and Zr
	Acetamide	Ti
	Hexamethylenetetraamine	Th
	Metal chelate and H_2O_2	Fe^{+3}
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 ß-hydroxy acetate)	Th and Fe^{+3}
	Ce^{+3} and bromate	Ce^{+4}
Carbonate	Trichloroacetate	Rare earths, Ba, and Ra
Chromate	Urea and dichromate	Ba and Ra
	Potassium cyanate and dichromate	Ba, Ra
	Cr^{+3} and bromate	Pb
Periodate	Acetamide	Pb
Chloride	Silver ammonia complex and ß-hydroxyethyl acetate	Ag
Arsenate	Arsenite and nitrite	Zr
Tetrachlorophthalate	Tetrachlorophthalic acid	Th
Dimethylglyoxime	Urea and metal chelate	Ni
8-Hydroxyquinoline	Urea and metal chelate	Al
Fluoride	Fluoroboric acid	La

Source: Salutsky, 1959.

- *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 Am in soil (DOE, 1990 and 1997, Method Am-01). After americium is coprecipitated with calcium oxalate (CaC_2O_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.

TABLE 14.12 — Influence of precipitation conditions on the purity of precipitates

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	+	+	+	○

*Symbols: +, increased purity; -, decreased purity; ○, little or no change in purity
Source: Salutsky, 1959.

14.8.4 Coprecipitation

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 ($RaSO_4$) 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, $BaSO_4$ (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 example, to determine ^{90}Sr in environmental samples, stable strontium (containing no radioisotopes of strontium) is added to increase the concentration of total strontium to the point that the common ion effect causes precipitation. 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, 1997, Method RP5001; DOE, 1990 and 1997, Method Sr-02; EPA, 1984, Sr-04). The term carrier is also used to designate the insoluble compound that causes coprecipitation. Barium sulfate, lanthanum fluoride (LaF_3), and strontium carbonate are sometimes referred to as the carrier in these coprecipitation procedures. See Wahl and Bonner (1951) for additional examples of tracers and their carriers used for coprecipitation.

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

14.8.4.1 Coprecipitation Processes

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

Inclusion. If coprecipitation is accomplished from a homogeneous solution allowing the crystals to form slowly in an orderly manner, then inclusion contributes to the coprecipitation process. Under these conditions, the logarithmic distribution law applies, which represents the most efficient coprecipitation method that involves mixed crystals (Salutsky, 1959):

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

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

Generally, λ decreases as the temperature increases; thus, coprecipitation by inclusion is favored by lower temperature.

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

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

where *I* represents the amount of impurity and *P* the amount of primary substance forming the precipitate. The symbol *D* is the homogeneous distribution coefficient. Values of *D* greater than one represent removal of a foreign ion by inclusion during coprecipitation. Some values of *D* can be found in Wahl and Bonner (1951). According to Hermann and Suttle (1961):

> "Homogeneous distribution is conveniently obtained at ordinary temperatures by rapid crystallization from supersaturated solutions with vigorous stirring. Under such conditions the precipitate first formed is very finely divided, the recrystallization of the minute crystals is rapid, and each molecule [sic] passes many times between solution and precipitate. If this process is repeated often enough, an equilibrium between solid and solution is obtained, and all the resulting crystals grow from a solution of constant composition."

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

Surface Adsorption. During surface adsorption, ions are adsorbed from solution onto the surfaces of precipitated particles. The conditions leading to surface adsorption are described by Salutsky (1959):

> "The surface of a precipitate is particularly active. Ions at the surface of a crystal (unlike those within the crystal) are incompletely coordinated and, hence are free to attract other ions of opposite charge from solution."

Adsorption involves a primary adsorption layer that is held very tightly, and a counter-ion layer held more loosely. Ions common to the precipitate are adsorbed most strongly at the surface to continue growth of the crystal. During precipitation of $BaSO_4$, barium ions (Ba^{+2}) and sulfate ions (SO_4^{-2}) are the primary ions adsorbed. If only one of the common ions remains in solution, then foreign ions of the opposite charge are adsorbed to maintain electrical neutrality. When barium sulfate is precipitated from a solution containing excess barium ions, for example, foreign ions such as Cl^{-1}, if present, are adsorbed after sulfate ions are depleted in the precipitation process. Foreign ions of the same charge, such as Na^{+1}, are repelled from the surface. Surface adsorption can be controlled, therefore, by controlling the concentration of ions during precipitation or by the addition of ions to alter the concentration. A precipitate of silver chloride (AgCl) in excess Ag^{+1} repels $^{212}Pb^{+2}$, but in a solution containing an equal quantity of the common silver and chloride ions, approximately 2 percent of ^{212}Pb is adsorbed (Salutsky, 1959). In contrast, almost 86 percent of ^{212}Pb is adsorbed if an iodide solution is added to precipitate the silver ions as silver iodide (AgI), thereby reducing the concentration of silver ions and making the chloride ion in excess in the solution. According to the Paneth-Fajans-Hahn adsorption rule, the ion most adsorbed will be the one that forms the least soluble compound with an ion of the precipitate. For example, barium sulfate in contact with a solution containing excess sulfate ions will adsorb ions of $Pb > Ca > K > Na$, which reflects the order of solubility of the respective sulfates: thus, $PbSO_4 < CaSO_4 < K_2SO_4 < Na_2SO_4$ (Salutsky, 1959).

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

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

Adsorption also depends on the concentration of an ion in solution (Berg, 1963). A high concentration of impurity increases the probability of solute interaction at the solid surface and favors adsorption. Salutsky (1959) comments on the percent adsorption:

> "Generally, the percent adsorption is much greater at low concentrations than at high concentrations. At very high concentrations of impurity, adsorption reaches a maximum value, i.e., the adsorption is saturated."

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

Mechanical entrapment occurs particularly when the precipitating agent is added directly to a solution. Because of the localized high concentrations of precipitant, impurities are precipitated that become occluded by the subsequent precipitation of the primary substance. The speed of the precipitation process also affects the extent of occlusion. Occlusion can be reduced, therefore, by homogeneous precipitation. Coprecipitation of strontium by barium sulfate, for example, is accomplished by the homogeneous generation of sulfate by the hydrolysis of dimethylsulfate, $(CH_3)_2SO_4$ (Hermann and Suttle, 1961). Digestion also eliminates occluded particles as the solid is recrystallized. Considerable occlusion occurs during nucleation, and, therefore, reducing the precipitation rate by lowering the temperature and reducing the number of nuclei formed reduces the initial coprecipitation by occlusion.

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

14.8.4.2 Water as an Impurity

In addition to other impurities, all precipitates formed from aqueous solutions contain water (Salutsky, 1959). This water might be essential water, present as an essential part of the chemical composition (e.g., $MgNH_4PO_4 \cdot 6H_2O$, $Na_2CO_3 \cdot H_2O$), or it might be nonessential water. Nonessential water can be present in the precipitate as hygroscopic water, surface water, or included water. Hygroscopic water refers to the water that a solid adsorbs from the surrounding atmosphere. Many colloidal precipitates are highly hygroscopic because of their large surface areas. Moreover, water can be adsorbed to the surface of the precipitate or included within the crystal matrix, as described previously.

14.8.4.3 Postprecipitation

Postprecipitation results when a solution contains two ions, one that is rapidly precipitated and another that is slowly precipitated by the precipitating agent (Kolthoff et al., 1969). The first precipitate is usually contaminated by the second one. For example, calcium oxalate is a moderately insoluble compound that can be precipitated quantitatively with time. Because the precipitation tends to be slow, the precipitate is allowed to remain in contact with the solution for some time before filtering. Magnesium oxalate is too soluble to precipitate on its own under normal conditions. As long as the solution contains a predominance of calcium ions, very little magnesium precipitates. However, as the precipitation of calcium approaches quantitative levels, the competition of calcium and magnesium ions for adsorption at the surface becomes more intense. As time progresses, the magnesium oxalate adsorbed on the surface acts as seed to induce the post-precipitation of a second solid phase of magnesium oxalate (MgC_2O_4). Once precipitated, the magnesium oxalate is only slightly soluble and does not redissolve.

14.8.4.4 Coprecipitation Methods

Selective coprecipitation of a radionuclide with an insoluble compound is primarily accomplished by the judicious selection of the compound that forms the precipitate and the concentration of solutions used in the precipitate's formation. Using good precipitation technique minimizes the coprecipitation of impurities. The compound, then, should maximize coprecipitation of the select radionuclide while providing a well-formed solid that attracts a minimum of other foreign ions as impurities. In general, conditions that favor precipitation of a substance in macroamounts also favor the coprecipitation of the same material from tracer concentrations (i.e., too low for precipitate formation) with a foreign substance (Friedlander et al., 1981). Wahl and Bonner (1951) provide a useful summary for coprecipitation of a tracer by a carrier:

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

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

The isolation of tracers often occurs in two steps: first the tracer is separated by coprecipitation with a carrier, and then it is separated from the carrier (Hermann and Suttle, 1961). Use of carriers that can be easily separated from the tracer is helpful, therefore, coprecipitation by inclusion is not generally used. Coprecipitation by surface adsorption on unspecific carriers is the most common method employed. Manganese dioxide MnO_2, sulfides (MnS), and hydroxides [$Mn(OH)_2$] are important nonspecific carriers because of their high surface areas. Ferric hydroxide [$Fe(OH)_3$] is very useful for adsorbing cations, because it forms a very finely divided precipitate with a negative charge in excess hydroxide ion. Ferric hydroxide is used, for example, to collect plutonium in solution after it has been isolated from tissue (DOE, 1990 and 1997, Method Pu-04). Tracers can be separated by dissolving the solid in acid and extracting the iron in ether (Hermann and Suttle, 1961).

> "The amount of ion adsorbed depends on its ability to compete with other ions in solution. Ions capable of displacing the ions of the radioelements are referred to as holdback carriers

> [see Section 14.9.2.4, "Holdback Carriers"]. Highly charged ions, chemical homologs, and ions isotopic with the radioelement are among the most efficient displacers. Thus, the addition of a little inactive strontium makes it possible to precipitate radiochemically pure radiobarium as the nitrate or chloride in the presence of radiostrontium."

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

TABLE 14.13 — Common coprecipitating agents for radionuclides(1)

Radionuclide	Oxidation State	Coprecipitate	Carrier(2)	Notes
Am	+3	hydroxide iodate fluoride, oxalate, phosphate, hydroxide oxalate acetate fluoride, sulfate acetate	Am^{+3}, Fe^{+3} Ce^{+4}, Th^{+4}, Zr^{+4} La^{+3}, Ce^{+3}, Nd^{+3}, Bi^{+3} Ca^{+2} Am^{+4} La^{+3} UO_2^{+2}	
Cs	+1	phosphomolybdate, chloroplatinate, bismuth nitrate, silicomolybdate	Cs^{+1}	
Co	+2	hydroxide potassium cobalt nitrate 1-nitroso-2-napthol sulfide	Co^{+2} Co^{+2} Co^{+2} Co^{+2}	
Fe	+3	hydroxide ammonium pyrouranate	Fe^{+3} Fe^{+3}	
I	−1	iodide	Pb^{+2}, Ag^{+1}, Pd^{+2}, Cu^{+2}	
Ni	+2	dimethylglyoxime hydroxide	Ni^{+2}	
Nb	(V)	hydroxide, phosphate	Nb(V)	
Np	+4	phosphate	Ca^{+2}	
Po	+4	tellurium tellurate selenium dioxide hydroxide sulfide	Te Pb^{+2} Se or Se^{-2} Mn^{+4} Fe^{+3}, Al^{+3}, La^{+3} Cu^{+2}, Bi^{+2}, Pb^{+2}	Tellurate reduced with $SnCl_2$
Pu	+3 +4 (VI)	fluoride sulfate fluoride oxalate, iodate phosphate sodium uranylacetate	La^{+3}, Nd^{+3}, Ce^{+3}, Ca^{+2} $La^{+3}(K^{+1})$ La^{+3}, Nd^{+3}, Ce^{+3} Th^{+4} Zr^{+2}, Bi^{+3} UO_2^{+2}	

Radionuclide	Oxidation State	Coprecipitate	Carrier(2)	Notes
Ra	+2	hydroxide	Fe^{+3}	
		sulfate, chromate, chloride, bromide	Ba^{+2}	
		oxalate, phosphate	Th^{+4}, Ca^{+2}, Ba^{+2}	
		fluoride	La^{+3}	
Sr	+2	carbonate	Sr^{+2}, Ba^{+2}, Ca^{+2}	
		nitrate	Sr^{+2}, Ba^{+2}	
		chromate	Ba^{+2}	Alkaline pH
		sulfate	Sr^{+2}, Ca^{+2}, Pb^{+2}	
		phosphate	Sr^{+2}	
		hydroxide	Fe^{+3}	
Tc	+4	hydroxide	Tc^{+4}, Fe^{+3}, Mn^{+2}	
	(VII)	chlorate, iodate, perruthenate, tetrafluoroborate	$(Phenyl)_4As^{+1}$	
		sulfide	Tc^{+7}, Re^{+7}, Cu^{+2}, Cd^{+2}	
Th	+4	hydroxide fluoride iodate phosphate, peroxide sulfate oxalate	Th^{+4}, La^{+3}, Fe^{+3}, Zr^{+3}, Ac^{+3}, Zn^{+2} Th^{+4}, La^{+3}, Nd^{+3}, Ce^{+3} Th^{+4}, Zr^{+3} Th^{+4}, Bi^{+3} Ba^{+2} Ca^{+2}	
U	+4	cupferron, pyrophosphate, phosphate, iodate, sulfate, oxalate	U^{+4}	
		fluoride	La^{+3}, Nd^{+3}	
	(V)	phosphate	Zr^{+3}	
		sulfate	Ca^{+2}	
	(VI)	cupferron	U(VI)	Neutral solution
		pyrouranate	U(VI)	From aqueous NH_3, many ions stay in solution as NH_3 complex
		phosphate	U(VI), Al^{+3}	
		peroxide	U(VI)	Th^{+4}, Zr^{+3} also coprecipitate
		hydroxide	Fe^{+3}	Without carbonate
		fluoride	Th^{+4}	
Zr	+4	hydroxide	Fe^{+3}	

(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 as the carrier, a different isotope would be used to assess recovery.

TABLE 14.14 — Coprecipitation behavior of plutonium and neptunium

Carrier Compound	Pu^{+3}	Pu^{+4}	Pu(VI)	Np^{+4}	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^{+4} hypophosphate		C	NC			
Oxalates:						
Lanthanum oxalate	C	C	NC	NC		
Bismuth oxalate	C	C	NC			
Thorium oxalate	C	C	NC	C		
U^{+4} 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		

"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.]

14.8.5 Colloidal Precipitates

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

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

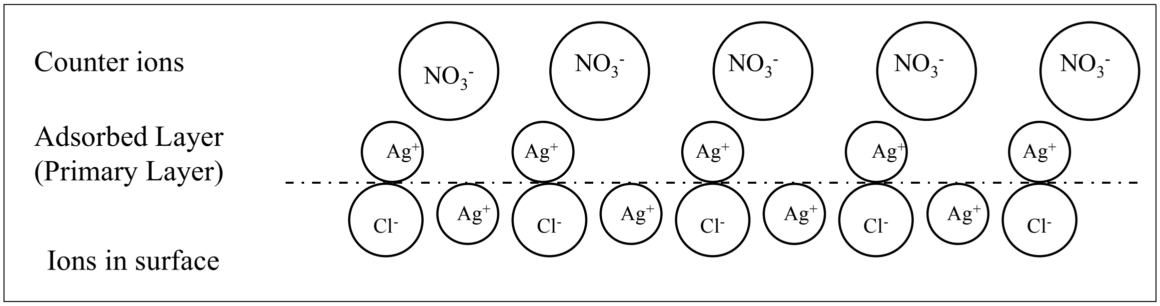


FIGURE 14.5 — The electrical double layer: A schematic representation of adsorption of nitrate counter-ions onto a primary adsorbed layer of silver ions at the surface of a silver chloride crystal (Peters et al., 1974).

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

Such adsorption of ions upon the surface of solids in solution is largely, but not entirely, based upon electrical attraction, otherwise adsorption would not be selective. Recall that there are four other factors, in addition to magnitude of charge, that affect the preferential adsorption by a colloid (see *Surface Adsorption* on page 14-72).

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

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

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

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

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

There are two types of colloidal solutions (Salutsky, 1959):

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

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

Colloidal precipitations can be a useful separation technique. Because of their great adsorption capacity, colloidal precipitates are excellent scavengers (collectors) for concentrating trace substances (Salutsky, 1959). Unspecific carriers such as manganese dioxide, sulfides and hydrated oxides are frequently used as scavengers. For example, protactinium can be efficiently scavenged and concentrated on manganese dioxide that is precipitated by adding a manganous salt to a solution containing permanganate. Ferric hydroxide is commonly used to scavenge cations (Section 14.8.4.4, “Coprecipitation Methods”). Moreover, scavenging precipitations can sometimes be used to remove interferences. For example, a radionuclide that is capable of existing in two oxidation states can be effectively purified by precipitation in one oxidation state, followed by scavenging precipitations for impurities, while the element of interest is in another oxidation state. A useful procedure for cerium purification involves repeated cycles of ceric iodate precipitation, reduction to Ce^{+3}, zirconium iodate [$Zr(IO_3)_4$] precipitation to remove impurities (with Ce^{+3} staying in solution), and reoxidation to Ce^{+4}.

14.8.6 Separation of Precipitates

The process of precipitation chemically separates an analyte from contaminants or other analytes. Precipitation generally is followed by one of two techniques that physically separates the precipitate: centrifugation or filtration.

Centrifugation is a technique that can be used for precipitates of many different physical forms. The best way to demonstrate the utility of centrifugation in radiochemical analyses is by example:

Example of Centrifugation

A method of radium analysis coprecipitates radium with barium using sulfuric acid to isolate the radium from its progeny. When the precipitation is completed, the mixture is centrifuged. The supernatant solution contains contaminants and radium progeny and is decanted. The precipitate is washed, *in situ*, with an isotonic sulfuric acid solution to maintain the insolubility of the precipitate, and to further enhance the removal of the contaminants. The mixture is re-centrifuged and the supernate again decanted.

This example demonstrates that centrifugation separates and purifies the precipitate without disturbing the mechanical flow of the separation process, and it minimizes the introduction of new contaminants by using the same glassware. It is noteworthy that there are several instances of using centrifugation to discard the precipitate and retain the supernate (e.g., the separation of barium from strontium using chromate). Separation by filtration at this point (not the final analytical step) would involve transfer onto and subsequent removal from the filter media. Filtration would be time consuming and risk low yield for the analysis. The speed and capacity of the centrifuge is dictated by the type of precipitate (e.g., gelatinous, crystalline, amorphous etc.), the sample size being processed, and the ancillary procedural steps to purify the precipitate.

The final separation of the analyte immediately preceding counting techniques is generally best suited by using filtration techniques. The physical nature of a precipitate not only affects the purity of the precipitate, but also the filterability of the precipitate. Large, well-formed crystals are desirable because they tend to contain fewer impurities, and are also easier to filter and wash. Many coagulated colloidal precipitates, such as hydrous oxides or sulfides, tend to form slimy aggregates and to clog the filter during filtration. There are several approaches that can be taken to improve the physical form of the precipitate (Salutsky, 1959):

- A trace quantity of a hydrophilic colloid can be added to produce complete and rapid flocculation. For example, gelatin has been used as a sensitizer in the precipitation of zinc sulfide, hydrous silica, and various other hydrous oxides, as well-coagulated, filterable precipitates (Salutsky, 1959).

- The slow precipitation techniques described in Section 14.8.3.2, “Factors Affecting Precipitation,” can be used to produce good precipitates.

- Aging the precipitate can result in a precipitate more amenable to filtration. During aging, small particles with a larger solubility go into solution, and larger particles grow at the cost of the smaller ones (see “Digestion” under Section 14.8.3.2, “Factors Affecting Precipitation”). Ostwald ripening results in a decrease in the number of particles and, therefore, a decrease in surface area. The speed of aging generally increases with temperature and with the increasing solubility of the precipitate in the aging media. Shaking can sometimes promote aging, perhaps by allowing particles to come into contact and to cement together.

14.8.7 Advantages and Disadvantages of Precipitation and Coprecipitation

14.8.7.1 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).
- Not energy- or resource-intensive compared to other techniques (e.g., solvent extraction).

14.8.7.2 Disadvantages

- Can be time consuming to digest, filter, 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.

14.9 Carriers and Tracers

14.9.1 Introduction

Radiochemical analysis frequently requires the radiochemist to separate and determine radionuclides that are present at extremely small quantities. The amount can be in the picomole range or less, at concentrations in the order of 10^{-15} to 10^{-11} molar. Analysis of radionuclides using counting techniques, such as alpha spectrometry, liquid scintillation, proportional counting, or gamma spectrometry, allows activities of radionuclides to be determined easily, even though the number of atoms (and mass percent) of these materials is vanishingly small. Table 14.15 identifies the number of atoms and mass present in several radionuclides, based on an activity of 500 dpm (8.33 Bq).

TABLE 14.15 — Atoms and mass of select radionuclides equivalent to 500 dpm

Radionuclide	Half-life*	Number of Atoms	Mass (g)
Radium-226	1,600 y	6.0×10^{11}	2.3×10^{-10}
Polonium-210	138.3 d	1.5×10^{8}	5.0×10^{-14}
Lead-212	10.6 h	4.5×10^{5}	1.6×10^{-16}
Thallium-208	3.1 min	2.3×10^{3}	8.0×10^{-19}

* Half-lives taken from Brookhaven National Laboratory, National Nuclear Science Database (www.nndc.bnl.gov/).

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

14.9.2 Carriers

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

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

14.9.2.1 Isotopic Carriers

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

The purpose of adding a carrier is to raise the chemical concentration of the analyte to the point where it can be separated using conventional techniques, but for the carrier to perform properly, it must have the same oxidation state and chemical form as the analyte. It is important then to add the carrier to the sample as early as possible in chemical process. For example, in the determination of ^{131}I in milk, the radioiodine might be present as I^{-1}, IO_3^{-1}, CH_3I, or I_2. The analyst should assume that all states are present, and treat the sample so that all atoms are brought to a common oxidation state and chemical form during some step in the procedure, before any separation takes place. If the final step is precipitation of AgI and the carrier is in the IO_3^{-1} form, no precipitate will form because $AgIO_3$ that forms when Ag^{+1} is added is relatively soluble compared to AgI. Furthermore, if separations of other radioisotopes are performed before this step, there is the possibility that quantities of the radioiodine could be trapped in the precipitate with other separated analytes. When concentrations of these materials are very small, even small losses are significant. The carrier also functions to prevent losses of the analyte during the separation of other radionuclides or interfering macro-contaminants. This is another reason that it is essential to add the carrier prior to any chemical treatment of the sample.

The laws of equilibrium for precipitation, distillation, complexation, and oxidation-reduction will apply to the entire chemical form of analyte in solution, both carrier and radioisotope. If, for example, 99.995 percent of all strontium is determined to be precipitated during a radiochemical procedure, then the amount of stable strontium remaining in solution will be 0.005 percent, which means that 0.005 percent of the radiostrontium still remains in the solution as well. Losses such as this occur during any chemical process. Frequently then, carriers are used in radiochemical analyses not only to raise the chemical concentration of the element, but also to determine the yield of the process. In order to determine the exact amount of radionuclide that was originally present in the sample, the yield (sometimes called the recovery) of the radionuclide collected at the end of the procedure should be known. However, because the amount of analyte at the start of the procedure is the unknown, the yield should be determined by an alternate method. The mass of the radioanalyte is insignificant in comparison to the carrier, and measuring the yield of the carrier (gravimetrically, for example) will allow the calculation of the yield of the analyte.

14.9.2.2 Nonisotopic Carriers

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

For several elements, nonisotopic carriers are chosen from a different family of elements, but they have the same ionic charge or similar crystalline morphology as the analyte. Lanthanum and neodymium as +3 ions are frequently used as nonisotopic carriers for U^{+4} and Pu^{+4} in their final separation as insoluble fluorides by the process of coprecipitation (Metz and Waterbury, 1962) (see also Section 14.8, "Precipitation and Coprecipitation"). The chemical form of the uranium and plutonium is particularly important for this process; the +4 oxidation state will coprecipitate, but the (VI) form will not. Uranium(VI) is present in solution as UO_2^{+2} and, therefore, will not be coprecipitated with lanthanum fluoride. However, it is very important to note that even though the precipitation of LaF_3 may be quantitative (i.e., >99.995 percent may be precipitated), there is no measure of how much uranium will also be coprecipitated. Because uranium and lanthanum are not chemically equivalent, the laws of solubility product constant for lanthanum cannot be applied to uranium. For these types of processes, separate methods, usually involving a tracer isotope of the analyte, should be used to determine the chemical yield of the process.

For alpha counting, rare-earth fluorides (such as NdF_3) are frequently used to coprecipitate the transuranic elements (Hindman, 1983 and 1986; Sill and Williams, 1981).

Another group of nonisotopic carriers can be described as general scavengers. Substances with high surface areas, or the ability to occlude contaminants in their floc, can be used to effect gross separation of all radionuclides from macro quantities of interfering ions. Ferric hydroxide, manganese dioxide (MnO_2) and sulfides (MnS), and hydrated oxides [$Mn(OH)_x$] are examples of these nonspecific carriers that have been used in many radiochemical separations to eliminate gross quantities of interfering substances.

14.9.2.3 Common Carriers

Carriers for specific analytes are discussed below.

Alkaline Earths

STRONTIUM AND BARIUM. Radioisotopes of Sr^{+2} and Ba^{+2} will coprecipitate with ferric hydroxide [$Fe(OH)_3$], while Ca^{+2} exhibits the opposite behavior and does not coprecipitate with ferric hydroxide. Lead sulfate ($PbSO_4$) will also carry strontium and barium.

Frequently, inactive strontium and barium are used as carriers for the radionuclides in order to facilitate separation from other matrix constituents and from calcium. The precipitates used most frequently in radiochemical procedures are the chromates (CrO_4^{-2}), nitrates (NO_3^{-1}), oxalates ($C_2O_4^{-2}$), sulfates (SO_4^{-2}), and barium chloride ($BaCl_2$). Several different methods of separation are identified here:

- Chromate precipitation is used in the classical separation of the alkaline earths. Barium chromate ($BaCrO_4$) is precipitated from a hot solution buffered to a pH of 4 to minimize strontium and calcium contamination of the barium precipitate. Ammonium ion (NH_4^{+1}) is then added to the solution, and strontium chromate ($SrCrO_4$) is precipitated.

- Barium and strontium can be separated from calcium as the nitrates. Fuming nitric acid is used to increase the nitric acid concentration to 60 percent, conditions at which barium and strontium nitrate [$Ba(NO_3)_2$ and $Sr(NO_3)_2$] precipitate and calcium does not.

- Oxalate precipitation does not separate one alkaline earth from another, but it is usually used to produce a weighable and reproducible form suitable for radioassay. The precipitation is accomplished from a basic solution with ammonium oxalate [$(NH_4)_2C_2O_4$].

- Barium sulfate ($BaSO_4$) precipitation is generally not used in separation procedures. It is more common as a final step to produce a precipitate that can be readily dried, weighed, and mounted for counting. Barium is readily precipitated by slowly adding dilute sulfuric acid (H_2SO_4) to a hot barium solution and digesting the precipitate. For the precipitation of strontium or calcium sulfate ($SrSO_4$ or $CaSO_4$), a reagent such as alcohol should be added to lower the solubility, and the precipitant must be coagulated by heat.

- Insolubility of barium chloride ($BaCl_2$) in strong hydrochloric acid solution (HCl) is the basis of the method to separate barium from calcium, strontium, and other elements. The precipitation is performed either by adding an ether-hydrochloric acid solution or by bubbling dry hydrogen chloride gas into the aqueous solution.

RADIUM. Radium yields the same types of insoluble compounds as barium: sulfates, chromates, carbonates (CO_3^{-2}), phosphates (PO_4^{-3}), oxalates, and sulfites (SO_3^{-2}). Hence, Ra coprecipitates with all Ba compounds and, to a lesser extent, with most Sr and Pb compounds. Barium sulfate and barium chromate are most frequently used to carry radium. Other compounds that are good carriers for radium include ferric hydroxide when precipitated at moderately high pH with sodium hydroxide (NaOH), barium chloride when precipitated from a cold mixed solvent of water and alcohol saturated with hydrochloric acid, barium iodate ($BaIO_3$) and various insoluble phosphates, fluorides and oxalates (e.g., thorium phosphate [$Th_3(PO_4)$], lanthanum fluoride (LaF_3), and thorium oxalate [$Th(C_2O_4)$].

Rare Earths, Scandium, Yttrium, and Actinium

Ferric hydroxide and calcium oxalate (CaC_2O_4) will coprecipitate radioisotopes of the rare earths without difficulty.

The rare earths will coprecipitate one with another in almost all of their reactions; one rare earth can always be used to coprecipitate another. The rare earth hydroxides, fluorides, oxalates, and 8-hydroxyquinolates in ammoniacal solution are insoluble. Conversely, the rare earth hydroxides will carry a number of elements that are insoluble in basic solution; the rare earth oxalate will coprecipitate calcium; and the rare earth fluorides tend to carry Ba and Zr. In the absence of macro quantities of rare earths, actinium will carry on barium sulfate and lead sulfate ($PbSO_4$).

Lead

Ferric hydroxide and aluminum hydroxide [$Al(OH)_3$] carry lead very effectively from ammonium solutions under a variety of conditions. Lead is carried by barium or radium chloride, but not carried by barium or radium bromide ($BaBr_2$ or $RaBr_2$). This behavior has been used to separate radiolead isotopes from radium salts. Lead is also carried by barium carbonate ($BaCO_3$), barium sulfate, radium sulfate, radium chloride, lanthanum carbonate [$La_2(CO)_3$], barium chloride, and silver chromate (Ag_2CrO_4). Calcium sulfate in the presence of alcohol has also been used to coprecipitate lead.

Polonium

Trace quantities of polonium are carried almost quantitatively by bismuth hydroxide [$Bi(OH)_3$] from ammoniacal solution. Ferric, lanthanum, and aluminum hydroxides have also been used as carriers for polonium in alkaline solutions. Colloidal platinum and coagulated silver hydroxide (AgOH) and ferric hydroxide sols have been used to carry polonium. Because of the high oxidation state of polonium, it is susceptible to being a contaminant in almost any precipitate. Removal of polonium by electrodeposition on nickel metal is recommended prior to final precipitation for any gross counting technique (proportional counting and liquid scintillation, for example).

Actinides

THORIUM. Thorium will coprecipitate with ferric, lanthanum [$La(OH)_3$], and zirconium hydroxide [$Zr(OH)_4$]. These hydroxide carriers are nonspecific, and therefore, will only remove thorium from a simple group of contaminants or as a group separation. The ferric hydroxide precipitation is best carried out at pH 5.5 to 6.

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

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

Coprecipitation of thorium on hydrogen hypophosphate (HPO_3^{-2}) or phosphate carriers can be performed from rather strongly acidic solutions. Zirconium phosphate [$Zr_3(PO_4)_4$] serves as a good carrier for trace levels of thorium. Moreover, thorium also will carry quantitatively on zirconium iodate from a strongly acidic solution. If coprecipitation is performed from a strongly acidic solution and the precipitate is washed with a solution containing iodate, the rare earths and actinium are eliminated. Cesium(+4) must be reduced to Ce^{+3} before precipitation so that it does not carry.

PROTACTINIUM. Protactinium will be carried quantitatively on hydroxide, carbonate, or phosphate precipitates of tantalum, zirconium, niobium, hafnium, and titanium. It is also carried by adsorption onto flocculent precipitates of calcium hydroxide [$Ca(OH)_2$)] or ferric hydroxide, and it is carried by manganese dioxide, which is produced by addition of potassium permanganate ($KMnO_4$) to a dilute nitric acid (HNO_3) solution containing manganese nitrate. However, titanium and zirconium are also carried under these conditions.

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

Uranium(+4) can be coprecipitated as the fluoride or phosphate [UF_4 or $U_3(PO_4)_4$] from relatively strong acid media; however, U(VI) phosphate [$(UO_2)_3(PO_4)_2$] is precipitated only from very weak acid solutions (pH 5 to 6) by the addition of carbonate-free ammonium. The rare earths, and other metals can also coprecipitate under these conditions.

In general, U^{+4} should behave similarly to Pu^{+4} and Np^{+4}, and should be carried by lanthanum fluoride, ceric and zirconium iodates [$Ce(IO_4)_3$ and $Zr(IO_3)_4$], cesium and thorium oxalates [$Th(C_2O_4)_2$], barium sulfate, zirconium phosphate [$Zr_3(PO_4)_4$], and bismuth arsenate ($BiAsO_4$). However, U(VI) does not carry with these agents as long as the concentration of either carrier or that of uranium is not too high.

PLUTONIUM AND NEPTUNIUM. Classically, plutonium and neptunium in their ter- and tetravalent oxidation states have been coprecipitated with lanthanum fluoride in the method most widely used for the isolation of femtograms of plutonium. However, large amounts of aluminum interfere with coprecipitation of plutonium, and other insoluble fluorides, such as the rare earths, calcium, and U^{+4}, coprecipitate.

AMERICIUM AND CURIUM. Bismuth phosphate ($BiPO_4$), which historically has been used to precipitate plutonium, will also carry americium and curium from 0.1–0.3 M nitric acid. Impurities such as calcium and magnesium are not carried under these conditions.

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

14.9.2.4 Holdback Carriers

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

14.9.2.5 Yield of Isotopic Carriers

The use of an isotopic carrier to determine the chemical yield (recovery) of the analyte is a critical step in the plan of a radiochemical analysis. The analytical method being used to determine the final amount of carrier will govern the method of separation. If a gravimetric method is to be used for the final yield determination, the precipitate must have all the characteristics that would be used for macro gravimetric analysis—easily dried, definite stoichiometry, nonhygroscopic, etc.

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

$$\text{Percent Yield} = \left[\frac{\text{mass of carrier in final separation step}}{\text{mass of carrier added}} \right] \times 100$$

It should be recognized that the element of interest is the only quantity used in this formula. For example, if strontium nitrate is used as the primary standard and strontium sulfate is the final precipitate, both masses should be corrected, using a gravimetric factor, so that only the mass of strontium is used in the equation in both the numerator and denominator.

Other methods to determine the yield of the carrier include atomic absorption spectrometry, ultraviolet/visible spectrometry, titrimetry, and potentiometry.

14.9.3 Tracers

The term "tracer"was used classically to express the concentration of any pure radionuclide in solution that had a mass too small to be measured by an analytical balance ($<10^{-5}$ to 10^{-6} g). More recently, the definition of a tracer has become more pragmatic. The current definition of a tracer is a known quantity of a radioisotope that is added to a solution of a chemically equivalent radioisotope of unknown concentration so that the yield of the chemical separation can be monitored. In general, a tracer is not a carrier, and a carrier is not a tracer.

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

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

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

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

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

Tracer analysis is very dependent upon the identical behavior of the tracer and the analyte. Therefore, tracers should be added to the system as early as possible, and complete isotopic exchange should be ensured as discussed previously (see Section 14.10, “Analysis of Specific Radionuclides”). Obvious difficulties arise when a tracer is added to a solid sample, especially if the sample is subdivided. Unless complete dissolution and isotopic exchange is ensured, results should be interpreted carefully.

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

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

- Technetium-99m, with a half-life of 6.02 h and a 143 keV gamma ray, is sometimes used as a yield monitor for ^{99}Tc determinations. Samples are counted immediately to determine the chemical recovery, then the ^{99m}Tc is allowed to decay before analysis of the ^{99}Tc.

- Europium-152 and ^{145}Sm are frequently used in the development of a new method to estimate the behavior of the +3 actinides and lanthanides.

- Tritium, ^{14}C, ^{32}P, and ^{36}Cl are frequently used in biological studies. In some of these studies, the radionuclide is covalently bonded to a molecule. As a result, the chemical behavior of the radionuclide will follow that of the molecule, not the element.

- Thorium-229 is used for Th determinations, both in alpha spectroscopy and inductively coupled plasma-mass spectroscopy (ICP-MS).

- Uranium-232 is commonly used as a tracer in alpha spectroscopy, whereas ^{233}U is used commonly for ICP-MS determinations. It should be noted that ^{232}U decays to ^{228}Th and therefore this needs to be taken into account when determining other alpha emitters.

- Plutonium-242 and ^{236}Pu are both used as tracers in Pu analyses. However, ^{236}Pu decays to ^{232}U, which needs to be taken into account when analyzing both Pu and U in the same sample aliquant.

- Americium-243 is employed in the analysis of ^{241}Am and Cm by alpha spectroscopy. It is assumed that Am and Cm are displaying similar chemical behavior.

14.9.3.1 Characteristics of Tracers

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

$$m \cdot UO_2^{+2} + p \cdot H_2O \rightarrow (UO_2)_m(OH)_p^{2m-p} + p \cdot H^{+1}$$

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

Interactions of radionuclides with impurities present special problems at low concentration. Difficulties include adsorption onto impurities such as dust, silica, or colloidal or suspended material, or adsorption onto the walls of the container. Generally, 10^{-8} to 10^{-7} moles are needed to cover a container's walls; but at tracer concentrations, much less is present (Choppin et al., 1995). Adsorption depends on (see *Surface Adsorption* on page 14-72):

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

- *Chemical State*. Adsorption increases with charge on the ion.

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

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

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

However, the adsorption process has been shown to be useful in some instances. For example, carrier-free Y^{+3} is quantitatively adsorbed onto filter paper from basic strontium solutions at concentrations at which yttrium hydroxide, $Y(OH)_3$, will not precipitate. Also, carrier-free Nb has been adsorbed on glass fiber filters for a fast specific separation technique (Friedlander et al., 1981).

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

14.9.3.2 Coprecipitation

Often, the concentration of tracer is so low that precipitation will not occur in the presence of a counter-ion that, at normal concentrations, would produce an insoluble salt. Under these conditions, carriers are used to coprecipitate the tracer (coprecipitation is described in Section 14.8.4).

14.9.3.3 Deposition on Nonmetallic Solids

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

Adsorption of radionuclides, with and without carriers (Friedlander et al., 1981), onto ion-exchange resins, followed by selective elution, has been developed into a very efficient separation technique (Wahl and Bonner, 1951) (see Section 14.7.4, "Ion-Exchange Chromatography"). Friedlander et al. (1981) illustrates this phenomenon:

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

14.9.3.4 Radiocolloid Formation

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

1. Sorption onto a preexisting colloidal impurity (approximately 0.001 to 0.5 μm), such as dust, cellulose fibers, glass fragments, organic material, and polymeric metal hydrolysis products (Adolff and Guillaumont, 1993; Choppin et al., 1995).

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

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

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

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

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

- Autoradiography reveals the formation of aggregates of radioactive atoms.

Several factors affect the formation of radiocolloids (Wahl and Bonner, 1951):

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

- *Foreign Particles.* The presence of foreign particles provides sites for the tracer to adsorb onto their surfaces. Ultrapure water prepared with micropore filters reduces the amount of foreign particles. However, the preparation of water that is completely free of suspended particles is difficult.

- *Electrolytes.* Electrolytes affect the nature (species) of the tracer ions in solution (see Section 14.10, "Analysis of Specific Radionuclides"), as well as the charge on both the radiocolloid and the foreign particle from which the colloid might have been derived.

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

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

14.9.3.5 Distribution (Partition) Behavior

Distribution (partition) coefficients, which reflect the behavior of solutes during solvent extraction procedures (Section 14.4, "Solvent Extraction"), are virtually independent of concentration down to tracer concentrations (Friedlander et al., 1981). Whenever the radioactive substance itself changes into a different form, however, the coefficient naturally changes, affecting the distribution between phases during extraction or any distribution phenomena, such as ion-exchange or gas-liquid chromatography (Section 14.7, "Chromatography"). Several properties of tracer solutions can alter the physical or chemical form of the radionuclide in solution and alter its distribution behavior (Wahl and Bonner, 1951):

- Radiocolloid formation might concentrate the radionuclide in the alternate phase or at the interface between the phases.

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

14.9.3.6 Vaporization

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

Vaporization of these amounts of materials from solid surfaces differs from the usual process of vaporization of macroamounts of material, because the surface of the solid is usually not completely covered with the radionuclide (Wahl and Bonner, 1951). Carrier-free radionuclides at the surface are bonded with the surface particles instead of with themselves, and the bonds broken during the process are between the solid and the radioisotope, rather than between the radioisotope particles themselves. Additionally, the nature of the radioisotope can be altered by trace quantities of gases such as oxygen and water present in the vacuum. Therefore, the identity of the radionuclide species vaporizing might be uncertain, and the data from the procedure can be hard to interpret. The rate of vaporization of radioisotopes also decreases with time, because the number of radioisotope particles available on the solid surface decreases with time.

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

14.9.3.7 Oxidation and Reduction

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

For a redox equilibrium such as:

$$PuO_2^{+2} + 4\ H^{+1} + Hg \rightarrow Pu^{+4} + Hg^{+2} + 2\ H_2O$$

the Nernst equation is used to calculate the redox potential, E, from the standard potential, E^0:

$$E = E^0 - kT\ \ln([Pu^{+4}][Hg^{+2}]/[PuO_2^{+2}][H^{+1}]^4)$$

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

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

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

14.10 Analysis of Specific Radionuclides

14.10.1 Basic Principles of Chemical Equilibrium

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

It is important to note that “chemical equilibrium” and “radioactive equilibrium” are two distinct phenomena that come together when performing chemical separations of radionuclides. See Attachment 14A at the end of this chapter for a thorough discussion of the phenomenon of “radioactive equilibrium.”

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

- A carrier of natural isotopic composition (i.e., the addition of stable strontium carrier to determine $^{89/90}$Sr; EPA, 1980, Method 905.0).

- A stable isotope tracer (i.e., enriched ^{18}O, ^{15}N, and ^{13}C, are frequently used in mass spectroscopy studies).

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

To achieve quantitative yields, there must be complete equilibration (isotopic exchange) between the added isotope and all the analyte species present. In the first example, isotopic exchange of the carrier with the radiostrontium is achieved and a weighable, stoichiometric compound of the carrier and radionuclide are produced. The chemical recovery from the separation technique is determined gravimetrically. Alternatively, a known quantity of a radioactive strontium isotope (i.e., ^{85}Sr) could be added and determined by the method appropriate for that analysis.

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

> “Fortunately, there are many reactions which have high exchange rates. This applies even to many heterogeneous systems, as in the heterogeneous catalysis of certain electron transfer reactions. In 1920, Hevesy, using ThB (^{212}Pb), demonstrated the rapid exchange between active lead nitrate and inactive lead chloride by the recrystallization of lead chloride from the homogeneously mixed salts. The ionization of these salts leads to the chemically identical lead ions, and a rapid isotopic exchange is expected. Similar reversible reactions account for the majority of the rapid exchange reactions observed at ordinary temperatures. Whenever possible, the analyst should conduct the isotope exchange reaction through a known reversible reaction in a homogeneous system. The true homogeneity of a system is not always obvious, particularly when dealing with the very low concentrations of the carrier-free isotopes. Even the usually well-behaved alkali-metal ions in carrier-free solutions will adsorb on the surfaces of their containment vessels or on colloidal and insoluble material in the solution. This is true especially in the heavier alkali metals, rubidium and cesium. Cesium ions in aqueous solution have been observed to absorb appreciably to the walls of glass vessels when the concentrations were below 10^{-6} g/mL.”

The reaction described above can be written as follows:

$$^{212}Pb(NO_3)_2(s) + PbCl_2(s) \rightarrow Pb(NO_3)_2 + {}^{212}PbCl_2$$

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

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

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

Crouthamel and Heinrich (1971) summarize the introduction to equilibration (isotopic exchange):

> "Probably the best way to give the reader a feeling for the ways in which isotopic exchange is achieved in practice is to note some specific examples from radiochemical procedures. The elements which show strong tendencies to form radiocolloids in many instances may be stabilized almost quantitatively as a particular complex species and exchange effected. Zirconium, for example, is usually exchanged in strong nitric acid-hydrofluoric acid solution. In this medium, virtually all the zirconium forms a ZrF_6^{-2} complex. Niobium exchange is usually made in an oxalate or fluoride acid medium. The exchange of ruthenium is accomplished through its maximum oxidation state, Ru(VIII) which can be stabilized in a homogeneous solution and distilled as RuO_4. Exchange may also be achieved by cycling the carrier through oxidation and reduction steps in the presence of the radioactive isotope. An iodine carrier with possible valence states of −1 to +7 is usually cycled through its full oxidation-reduction range to ensure complete exchange. In a large number of cases, isotopic exchange is not a difficult problem; however, the analyst cannot afford to relax his attention to this important step. He must

> consider in each analysis the possibility of both the slow exchange of certain chemical species in homogenous solution and the possible very slow exchange in heterogeneous systems. In the latter case, this may consist simply of examining the solutions for insoluble matter and taking the necessary steps to either dissolve or filter it and to assay for possible radioactive content."

Also see the discussion of equilibration of specific radionuclides in Section 14.10.9, "Review of Specific Radionuclides."

14.10.2 Oxidation State

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

14.10.3 Hydrolysis

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

$$Ra^{+2} + x\cdot H_2O \rightarrow Ra(H_2O)_x^{+2}$$

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

$$M^{+n} + m\cdot H_2O \rightarrow M(OH)_m^{+(n-m)} + m\cdot H^{+1}$$

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

$$Fe^{+3} + H_2O \rightarrow Fe(OH)^{+2} + H^{+1}$$

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

$$M(OH_2)_x^{+n} \rightarrow M(OH_2)_{x-1}(OH)^{(n-1)+} + H^{+1}$$

In the latter equation, the hydrated complex ion associated with the hydroxide ion, is known as the aquo-hydroxo species (Birkett et al., 1988). As each equation indicates, hydrolysis increases the acidity of the solution, and the concentration of the hydrogen ion (pH) affects the position of equilibrium. An increase in acidity (increase in H^{+1} concentration; decrease in pH) shifts the position of equilibrium to the left, decreasing hydrolysis, while a decrease in acidity shifts it to the right, increasing hydrolysis. The extent of hydrolysis, therefore, depends on the pH of the solution containing the radionuclide. The extent of hydrolysis is also influenced by the radius and charge of the cation (charge/radius ratio). Generally, a high ratio increases the tendency of a cation to hydrolyze. A ratio that promotes hydrolysis is generally found in small cations with a charge greater than one (Be^{+2}, for example). The Th^{+4} cation, with a radius three times the size of the beryllium ion but a +4 charge, is hydrolyzed extensively, even at a pH of four (Baes and Mesmer, 1976). It is not surprising, therefore, that hydrolysis is an especially important factor in the behavior of several metallic radionuclides in solution, and is observed in the transition, lanthanide, and actinide groups. For the actinide series, the +4 cations have the greatest charge/radius ratio and undergo hydrolysis most readily. Below pH 3, the hydrolysis of Th^{4+} is negligible, but at higher pH, extensive hydrolysis occurs. Uranium (+4) undergoes hydrolysis in solution at a pH above 2.9 with $U(OH)_3^+$ being the predominant hydrolyzed species. Neptunium ions undergo hydrolysis in dilute acid conditions with evidence of polymer formation in acidic solutions less than 0.3 M. The hydrolysis of plutonium is the most severe, often leading to polymerization (see Section 14.10.4, “Polymerization”). In summary, the overall tendency of actinides to hydrolyze decreases in the order (Katz et al., 1986):

$$An^{+4} > AnO_2^{+2} > An^{+3} > AnO_2^{+1}$$

where “An” represents the general chemical symbol for an actinide.

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

$$U^{+4} + H_2O \rightarrow U(OH)^{+3} + H^{+1}$$

$$U(OH)^{+3} + H_2O \rightarrow U(OH)_2^{+2} + H^{+1}$$

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

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

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

Thus, a knowledge of the identity and stability of radionuclide ion hydrolysis products is important in understanding or predicting the chemical behavior of trace quantities of radionuclides in solution (Baes and Mesmer, 1976). As the equilibrium equation indicates, H^{+1} is produced as cations hydrolyze. Undesirable consequences of hydrolysis can, therefore, be minimized or eliminated by the addition of acid to the analytical mixture to reverse hydrolysis or prevent it from occurring. Numerous steps in radioanalytical procedures are performed at low pH to eliminate hydrolytic effects. It is also important to know the major and minor constituents of any sample, because hydrolysis effects are a function of pH and metal concentration. Thus, maintaining the pH of a high iron-content soil sample below pH 3.0 is important, even if iron is not the analyte.

14.10.4 Polymerization

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

$$2\ M(H_2O)_{x-1}(OH)^{+(n-1)} \rightarrow [(H_2O)_{x-2}M(OH)_2M(H_2O)_{x-2}]^{+2(n-1)} + 2\ H_2O$$

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

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

> "Increasing the pH of a metal ion solution, by shifting the position of hydrolysis equilibrium ..., results in an increased concentration of hydrolyzed species ..., which in turn causes increased formation of polymeric species ... . Diluting a solution has two opposing effects on the formation of polymeric species:
>
> "(1) Because dilution of acidic solutions causes a decrease in H^{+1} concentration (i.e., an increase in pH), it causes a shift in the hydrolyzed equilibrium toward formation of hydrolyzed species.
>
> "(2) On the other hand, dilution decreases the ratio of polymeric to monomeric complexes in solution. For metals that form both monomeric and polymeric complexes, this means that monomeric species predominate beyond a certain level of dilution."

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

14.10.5 Complexation

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

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

14.10.6 Radiocolloid Interference

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

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

Crouthamel and Heinrich (1971) provide some specific insight into radiocolloidal interference in the equilibration problem:

> "The transition metals tend to form radiocolloids in solution, and in these heterogeneous systems the isotopic exchange reaction between a radiocolloid and inactive carrier added to the solution is sometimes slow and, more often, incomplete. Elements which show a strong tendency to form radiocolloids, even in macro concentrations and acid solutions, are titanium, zirconium, hafnium, niobium, tantalum, thorium, and protactinium, and, to a lesser degree, the rare earths. Other metals also may form radiocolloids, but generally offer a wider choice of valence states which may be stabilized in aqueous solutions"

14.10.7 Isotope Dilution Analysis

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

> "Specific activity is defined as the ratio of the number of radioactive atoms to the total number of atoms of a given element in the sample (N^*/N). In many cases where only the ratios of specific activities are needed, quantities proportional to N^*/N, such as activity/mole, are referred to as specific activity."

Isotope dilution analysis uses a known amount of radionuclide to determine an unknown mass of stable nuclide of the same element. For example, isotope dilution can be used to determine the amount of some inactive material A in a system (Wang et al., 1975). To the system containing x grams of an unknown weight of the inactive form of A, y grams of active material A^* of known activity D is added. The specific activity of the added active material, S_1, is given by:

$$S_1 = D/y$$

After ensuring isotopic exchange, the mixture of A and A^* is isolated, but not necessarily quantitatively, and purified. The specific activity, S_2, is measured. Due to the conservation of matter,

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

and by substituting for S_1y for D and rearranging, the amount x of inactive A is given as

$$x = y\,(S_1/S_2 - 1)$$

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

14.10.8 Masking and Demasking

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

$$A + Ms \rightarrow A \cdot Ms$$

where *A* is the normal reacting molecule or ion, and *Ms* is the masking agent. The decreased concentration of *A* at equilibrium determines the efficiency of masking. An excess of masking agent favors the completeness of masking, as expected from LeChatelier's Principle. Feigl (1936) has described masking reagent and the masking of a reaction:

> "... the concentration of a given ion in a solution can be so diminished by the addition of substances which unite with the ion to form complex salts that an ion product sufficient to form a precipitate or cause a color reaction is no longer obtained. Thus we speak of the masking of a reaction and call the reagent responsible for the disappearance of the ions necessary for the reaction, the masking reagent."

The concepts of masking and demasking are discussed further in Perrin (1979) and in Dean (1995).

Masking techniques are frequently used in analytical chemistry because they often provide convenient and efficient methods to avoid the effects of unwanted components of a system without having to separate the interferent physically. Therefore, the selectivity of many analytical techniques can be increased through masking techniques. For example, copper can be prohibited from carrying on ferric hydroxide at pH 7 by the addition of ammonium ions to complex the copper ions. Fe^{3+} and Al^{3+} both interfere with the extraction of the +3 actinides and lanthanides in some systems, but Fe^{3+} can be easily masked through reduction with ascorbic acid, and Al^{3+} can be masked through complexation with fluoride ion (Horwitz et al., 1993 and 1994). In another example, uranium can be isolated on a U/TEVA® column (Eichrom Technologies, Inc., Darien, IL) from nitric acid solutions by masking the tetravalent actinides with oxalic acid; the tetravalent actinides are complexed and pass through the column, whereas uranium is extracted (SpecNews, 1993). Strontium and barium can be isolated from other metals by cation exchange from a solution of water, pyridine, acetic acid and glycolic acid. The other metals form neutral or negative complexes and pass through the cation column, while strontium and barium are retained (Orlandini, 1972). Masking phenomena are present in natural systems as well. It has been demonstrated that humic and fulvic acids can complex heavy metals such that they are no longer bioavailable and are, therefore, not taken up by plants. Tables 14.16 and 14.17 list common masking agents.

TABLE 14.16 — Masking agents for ions of various metals

Metal	Masking Agent
Ag	Br^-, citrate, Cl^-, CN^-, I^-, NH_3, SCN^- $S_2\,O_3^{-2}$, thiourea, thioglycolic acid, diethyldithiocarbamate, thiosemicarbazide, bis(2−hydroxyethyl)dithiocarbamate
Al	Acetate, acetylacetone, BF_4^-, citrate, $C_2O_4^{-2}$, EDTA, F^-, formate, 8-hydroxyquinoline-5-sulfonic acid, mannitol, 2,3-mercaptopropanol, OH^-, salicylate, sulfosalicylate, tartrate, triethanolamine, tiron
As	Citrate, 2,3-dimercaptopropanol, $NH_2OH{\cdot}HCl$, OH^-, S_2^{-2}, tartrate
Au	Br^-, CN^-, NH_3, SCN^-, $S_2O_3^{-2}$, thiourea
Ba	Citrate, cyclohexanediaminetetraacetic acid, *N,N*-dihydroxyethylglycine, EDTA, F^-, SO_4^{-2}, tartrate
Be	Acetylacetone, citrate, EDTA, F^-, sulfosalicylate, tartrate
Bi	Citrate, Cl^-, 2,3-dimercaptopropanol, dithizone, EDTA, I^-, OH^-, $Na_5P_3O_{10}$, SCN^-, tartrate, thiosulfate, thiourea, triethanolamine
Ca	BF_4^-, citrate, *N,N*-dihydroxyethylglycine, EDTA, F^-, polyphosphates, tartrate
Cd	Citrate, CN^-, 2,3-dimercaptopropanol, dimercaptosuccinic acid, dithizone, EDTA, glycine, I^-, malonate, NH_3, 1,10-phenanthroline, SCN^-, $S_2O_3^{-2}$, tartrate
Cs	Citrate, *N,N*-dihydroxyethylglycine, EDTA, F^-, PO_4^{-3}, reducing agents (ascorbic acid), tartrate, tiron
Co	Citrate, CN^-, diethyldithiocarbamate, 2,3−dimercaptopropanol, dimethylglyoxime, ethylenediamine, EDTA, F^-, glycine, H_2O_2, NH_3, NO_2^-, 1,10-phenanthroline, $Na_5P_3O_{10}$, SCN^-, $S_2O_3^{-2}$, tartrate
Cr	Acetate, (reduction with) ascorbic acid + KI, citrate, *N,N*-dihydroxyethylglycine, EDTA, F^-, formate, $NaOH + H_2O_2$, oxidation to CrO_4^{-2}, $Na_5P_3O_{10}$, sulfosalicylate, tartrate, triethylamine, tiron
Cu	Ascorbic acid + KI, citrate, CN^-, diethyldithiocarbamate, 2,3-dimercaptopropanol, ethylenediamine, EDTA, glycine, hexacyanocobalt(III)(3^-), hydrazine, I^-, NaH_2PO_2, $NH_2OH{\cdot}HCl$, NH_3, NO^-_2, 1,10-phenanthroline, S^{-2}, $SCN^- + SO_3^{-2}$, sulfosalicylate, tartrate, thioglycolic acid, thiosemicarbazide, thiocarbohydrazide, thiourea
Fe	Acetylacetone, (reduction with) ascorbic acid, $C_2O_4^{-2}$, citrate, CN^- 2,3-dimercaptopropanol, EDTA, F^-, NH_3, $NH_2OH{\cdot}HCl$, OH^-, oxine 1,10-phenanthroline, 2,2'-bipyridyl, PO_4^{-3}, $P_2O_7^{-4}$, S^{-2}, SCN^-, $SnCl_2$, $S_2O_3^{-2}$, sulfamic acid, sulfosalicylate, tartrate, thioglycolic acid, thiourea, tiron, triethanolamine, trithiocarbonate
Ga	Citrate, Cl^-, EDTA, OH^-, oxalate, sulfosalicylate, tartrate
Ge	F^-, oxalate, tartrate
Hf	See Zr
Hg	Acetone, (reduction with) ascorbic acid, citrate, Cl^-, CN^-, 2,3-dimercaptopropan-1-ol, EDTA, formate, I^-, SCN^-, SO_3^{-2}, tartrate, thiosemicarbazide, thiourea, triethanolamine
In	Cl^-, EDTA, F^-, SCN^-, tartrate thiourea, triethanolamine
Ir	Citrate, CN^-, SCN^-, tartrate, thiourea

Metal	**Masking Agent**
La	Citrate, EDTA, F^-, oxalate, tartrate, tiron
Mg	Citrate, $C_2O_4^{-2}$, cyclohexane-1,2-diaminetetraacetic acid, *N,N*-dihydroxyethylglycine, EDTA, F^-, glycol, hexametaphosphate, OH^-, $P_2O_7^{-4}$, triethanolamine
Mn	Citrate, CN^-, $C_2O_4^{-2}$, 2,3–dimercaptopropanol, EDTA, F^-, $Na_5P_3O_{10}$, oxidation to MnO_4^-, $P_2O_7^{-4}$, reduction to Mn^{+2} with $NH_2OH{\cdot}HCl$ or hydrazine, sulfosalicylate, tartrate, triethanolamine, triphosphate, tiron
Mo	Acetylacetone, ascorbic acid, citrate, $C_2O_4^{-2}$, EDTA, F^-, H_2O_2, hydrazine, mannitol, $Na_5P_3O_{10}$, $NH_2OH{\cdot}HCl$, oxidation to molybdate, SCN^-, tartrate, tiron, triphosphate
Nb	Citrate, $C_2O_4^{-2}$, F^-, H_2O_2, OH^-, tartrate
Nd	EDTA
NH_4^+	HCHO
Ni	Citrate, CN^-, *N,N*-dihydroxyethylglycine, dimethylglyoxime, EDTA, F^-, glycine, malonate, $Na_5P_3O_{10}$,
	NH_3 1,10-phenanthroline, SCN^-, sulfosalicylate, thioglycolic acid, triethanolamine, tartrate
Np	F^-
Os	CN^-, SCN^-, thiourea
Pa	H_2O_2
Pb	Acetate, $(C_6H_5)_4AsCl$, citrate, 2,3-dimercaptopropanol, EDTA, I^-, $Na_5P_3O_{10}$, SO_4^{-2}, $S_2O_3^{-2}$, tartrate, tiron, tetraphenylarsonium chloride, triethanolamine, thioglycolic acid
Pd	Acetylacetone, citrate, CN^-, EDTA, I^-, NH_3, NO_2^-, SCN^-, $S_2O_3^{-2}$, tartrate, triethanol-amine
Pt	Citrate, CN^-, EDTA, I^-, NH_3, NO_2^-, SCN^-, $S_2O_3^{-2}$, tartrate, urea
Pu	Reduction to Pu^{+4} with sulfamic acid
Rare Earths	$C_2O_4^{-2}$, citrate, EDTA, F^-, tartrate
Re	Oxidation to perrhenate
Rh	Citrate, tartrate, thiourea
Ru	CN^-, thiourea
Sb	Citrate, 2,3-dimercaptopropanol, EDTA, I^-, OH^-, oxalate, S^{-2}, S_2^{-2}, $S_2O_3^{-2}$, tartrate, triethanolamine
Sc	Cyclohexane-1,2-diaminetetraacetic acid, F^-, tartrate
Se	Citrate, F^-, I^-, reducing agents, S^{-2}, SO_3^{-2}, tartrate
Sn	Citrate, $C_2O_3^{-2}$, 2,3-dimercaptopropanol, EDTA, F^-, I^-, OH^-, oxidation with bromine water, PO_4^{-3}, tartrate, triethanolamine, thioglycolic acid
Ta	Citrate, F^-, H_2O_2, OH^-, oxalate, tartrate
Te	Citrate, F^-, I^-, reducing agents, S^{-2}, sulfite, tartrate
Th	Acetate, acetylacetone, citrate, EDTA, F^-, SO_4^{-2}, 4-sulfobenzenearsonic acid, sulfosalicylic acid, tartrate, triethanolamine
Ti	Ascorbic acid, citrate, F^-, gluconate, H_2O_2, mannitol, $Na_5P_3O_{10}$, OH^-, SO_4^{-2}, sulfosalicylic, acid, tartrate, triethanolamine, tiron
Tl	Citrate, Cl^-, CN^-, EDTA, HCHO, hydrazine, $NH_2OH{\cdot}HCl$, oxalate, tartrate, triethanolamine
U	Citrate, $(NH_4)_2CO_3$, $C_2O_4^{-2}$, EDTA, F^-, H_2O_2, hydrazine + triethanolamine, PO_4^{-3}, tartrate
V	(reduction with) Ascorbic acid, hydrazine, or $NH_2OH{\cdot}HCl$, CN^-, EDTA, H_2O_2, mannitol, oxidation to vanadate, triethanolamine, tiron

Metal	Masking Agent
W	Citrate, F^-, H_2O_2, hydrazine, $Na_5P_3O_{10}$, $NH_2OH \cdot HCl$, oxalate, SCN^-, tartrate, tiron, triphosphate, oxidation to tungstate
Y	Cyclohexane-1,2-diaminetetraacetic acid, F^-
Zn	Citrate, CN^-, *N,N*–dihydroxyethylglycine, 2,3-dimercaptopropanol, dithizone, EDTA, F^-, glycerol, glycol, hexacyanoferrate(II)(4^-), $Na_5P_3O_{10}$, NH_3, OH^-, SCN^-, tartrate, triethanolamine
Zr	Arsenazo, carbonate, citrate, C_2O^{-2}, cyclohexane-1,2-diaminetetraacetic acid, EDTA, F^-, H_2O_2, PO_4^{-3}, $P_2O_7^{-4}$, pyrogallol, quinalizarinesulfonic acid, salicylate, $SO_4^{-2} + H_2O_2$, sulfosalicylate, tartrate, triethanolamine

Sources: Perrin (1979) and Dean (1995)

TABLE 14.17 — Masking agents for anions and neutral molecules

Anion or Neutral Molecule	Masking Agent
Boric Acid	F^-, glycol, mannitol, tartrate, and other hydroxy acids
Br^-	Hg^{+2}
Br_2	Phenol, sulfosalicylic acid
BrO_3^-	Reduction with AsO_4^{-5}, hydrazine, sulfite, or thiosulfate
Chromate(VI)	Reduction with AsO_4^{-5}, ascorbic acid, hydrazine, hydroxylamine, sulfite, or thiosulfate
Citrate	Ca^{+2}
Cl^-	Hg^{+2}, Sb^{+3}
Cl_2	Sulfite
ClO_3^-	Thiosulfate
ClO_4^-	Hydrazine, sulfite
CN^-	HCHO, Hg^{+2}, transition-metal ions
EDTA	Cu^{+2}
F^-	Al^{+3}, Be^{+2}, boric acid, Fe^{+3}, Th^{+4}, Ti^{+4}, Zr^{+4}
$Fe(CN)_3^{-3}$	AsO_4^{-5}, ascorbic acid, hydrazine, hydroxylamine, thiosulfate
Germanic Acid	Glucose, glycerol, mannitol
I^-	Hg^{+2}
I_2	Thiosulfate
IO_3^-	Hydrazine, sulfite, thiosulfate
IO_4^-	AsO_4^{-5}, hydrazine, molybdate(VI), sulfite, thiosulfate
MnO_4^-	Reduction with AsO_4^{-5}, ascorbic acid, azide, hydrazine, hydroxylamine, oxalic acid, sulfite, or
MoO_4^{-2}	thiosulfate
NO_2^-	Citrate, F^-, H_2O_2, oxalate, thiocyanate + Sn^{+2}
Oxalate	Co^{+2}, sulfamic acid, sulfanilic acid, urea
Phosphate	Molybdate(VI), permanganate, Al^{+3}
S	Fe^{+3}, tartrate
S^{-2}	CN^-, S^{2-}, sulfite
Sulfate	Permanganate + sulfuric acid, sulfur
Sulfite	Cr^{+3} + heat
SO_6^{-2}	HCHO, Hg^{+2}, permanganate + sulfuric acid
Se and its anions	Ascorbic acid, hydroxylamine, thiosulfate
TeI^-	Diaminobenzidine, sulfide, sulfite

Anion or Neutral Molecule	**Masking Agent**
Tungstate	Citrate, tartrate
Vanadate	Tartrate

Sources: Perrin (1979) and Dean (1995)

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^{4+} or Mo^{6+}, and hydroxide is used to demask the thiocyanate complexes of Fe^{3+}. In addition, it might be possible to destroy the masking agent in solution through a chemical reaction (i.e., through the oxidation of EDTA in acidic solutions by permanganate or another strong oxidizing agent).

14.10.9 Review of Specific Radionuclides

The analytical separation and analysis of radionuclides involves several scientific disciplines. The decay of one radionuclide to another is referred to as “radioactive equilibrium.” A series of mathematical expressions (derived from the Bateman equations, Friedlander et al., 1981) identify three separate cases of these equilibria (see Attachment 14A, “Radioactive Decay and Equilibrium”).

14.10.9.1 Americium

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

<u>Isotopes</u>

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

Occurrence

None of the isotopes of americium occur naturally. It is produced synthetically by neutron bombardment of ^{238}U or ^{239}Pu followed by beta decay of the unstable intermediates. Americium-241 is found in various plutonium wastes and can be extracted from reactor wastes. Some industrial ionization sources also contain americium. Decay of ^{241}Pu injected in the atmosphere during weapons testing contributes to the presence of ^{241}Am.

The silver metal is prepared by reduction of americium fluoride (AmF_3) or americium oxide (AmO_2) with active metals at high temperatures and is purified by fractional distillation, taking advantage of its exceptionally high vapor pressure compared to other transuranium elements. Kilogram quantities of ^{241}Am are available, but only 10 to 100 g quantities of ^{243}Am are prepared.

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

Solubility of Compounds

Among the soluble salts are the nitrate, halides, sulfate, and chlorate of americium (Am^{+3}). The fluoride, hydroxide, and oxalate are insoluble. The phosphate and iodate are moderately soluble in acid solution. Americium(VI) is precipitated with sodium acetate to produce the hydrate, $NaAmO_2(C_2H_3O_2)_3 \cdot xH_2O$.

Review of Properties

The study of the properties of americium is very difficult because of the intense alpha radiation emitted by ^{241}Am and ^{243}Am, but some properties are known. Americium metal is very ductile and malleable but highly reactive and unstable in air, forming the oxide. It is considered to be a slightly more active metal than plutonium and is highly reactive combing directly with oxygen, hydrogen, and halides to form the respective compounds, AmO_2, AmH_3, and AmX_3. Alloys of americium with platinum, palladium, and iridium have been prepared by hydrogen reduction of americium oxide in the presence of the finely divided metals.

Unless the transuranium elements are associated with high-level gamma emission, the principal toxicological problems associated with the radionuclides are the result of internal exposure after inhalation or ingestion. When inhaled or ingested, they are about equally distributed between bone tissue and the liver. At high doses transuranics lead to malignant tumors years later. In addition, large quantities of ^{241}Am could conceivably lead to criticality problems, producing external radiation hazards or neutron exposure from (α,n) reactions. Americium-241 is also a gamma emitter.

Americium is generally thought to be adsorbed by many common minerals at pH values found in the environment. Complexation of Am^{+3} by naturally occurring ligands, however, would be expected to strongly reduce its adsorption.

Solution Chemistry

Americium can exist in solution in the +3, +4, (V), and (VI) oxidation states. Simple aqueous ions of Am^{+3} and AmO_2^{+2} (VI oxidation state) are stable in dilute acid, but Am^{+3} is the predominant oxidation state. Free radicals produced by radiolysis of water by alpha particles reduce the higher states spontaneously to Am^{+3}. The +3 oxidation state exists as $Am(OH)_3$ in alkaline solution. Simple tetravalent americium is unstable in mineral acid solutions, disproportionating rapidly to produce Am^{+3} and AmO_2^{+1} [Am(V)] in nitric and perchloric acid solutions. In contrast, dissociation of $Am(OH)_4$ or AmO_2 [both Am^{+4}] in sulfuric acid solutions produces solutions containing Am^{+3} and AmO_2^{+2}. Stability is provided by complexation with fluoride ions and oxygen-containing ligands such as carbonate and phosphate ions. The AmO_2^{+1} ion also disproportionates in acid solutions to yield Am^{+3} and AmO_2^{+2}, but the process for ^{241}Am is so slow that radiation-induced reduction dominates. Evidence exists for the presence of Am(VII) in alkaline solutions from the oxidation of AmO_2^{+2}.

OXIDATION-REDUCTION BEHAVIOR. Although disproportionation reactions convert the +4 and (V) oxidation states into the +3 and (VI) states, radiolysis eventually converts the higher oxidation state into Am^{+3}. Redox processes are used, however, to produce solutions of alternate oxidation states and to equilibrate the forms of americium into a common state, usually +3, but sometimes (VI).

The +4 state is reduced to Am^{+3} by iodide. In dilute, nonreducing solutions, peroxydisulfate ($S_2O_8^{-2}$) oxidize both the +3 and (V) states to the (VI) state. Ce^{+4} and ozone (O_3) oxidize the (V) state to (VI) in perchloric acid solution. Electrolytic oxidation of Am^{+3} to AmO_2^{+2} occurs in phosphoric, nitric, and perchloric acid solutions and solutions of sodium bicarbonate (Na_2CO_3). The latter ion is reduced to Am^{+3} by iodide, hydrogen peroxide, and the nitrite ion (NO_2^{-1}).

COMPLEXATION. The +3 oxidation state forms complexes in the following order of strength (in aqueous solution): $F^- > H_2PO_4^- > SCN^- > NO_3^- > Cl^-$. Both Am^{+3} and Am^{+4} form complexes with organic chelants. These are stable in aqueous and organic solvents. Americium (+4) can be easily reduced unless special oxidizing conditions are maintained. The AmO_2^{+2} ion also forms significant complex ions with nitrate, sulfate, and fluoride ions.

HYDROLYSIS. The actinide elements are known for their tendency to hydrolyze and, in many cases, form insoluble polymers. In the predominant +3 oxidation state in solution, americium, with its large radius, has the least tendency of the +3 actinides to hydrolyze; yet, hydrolysis is expected to occur with some polymerization. Hydrolysis that does occur is complicated and depends on the nature of the cations present and may start at pH values as low as 0.5–1.0. In contrast, the AmO_2^{+2}, like all actinyl ions, undergoes hydrolysis to an appreciable extent. The tendency to form polymers of colloidal dimensions, however, appears to be small relative to other actinide ions in the (VI) oxidation state. Precipitation occurs early on after relatively small polymeric aggregates form in solution. The strong tendency to form insoluble precipitates after a small amount of hydrolysis makes characterization of the water-soluble polymers a difficult problem.

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

Dissolution of Samples

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

Separation Methods

The separation of americium, particularly from other transuranics, is facilitated by the exceptional stability of Am^{+3} compared to the trivalent ions of other actinides, which more readily convert to higher oxidation states under conditions that americium remains trivalent.

PRECIPITATION AND COPRECIPITATION. Coprecipitation with lanthanum fluoride (LaF_3) is achieved after reduction of higher oxidation states to Am^{+3}. Select oxidation of other transuranic elements such as neptunium and plutonium to the +4 or VI oxidation states solubilizes these radionuclides leaving americium in the insoluble form. Although coprecipitation with rare earths as fluorides or hydroxides from a bicarbonate solution of americium(VI), is used to purify americium, it is not as effective as ion-exchange procedures. Other coprecipitating agents for Am^{+3} include thorium oxalate [$Th(C_2O_4)_2$], calcium oxalate (CaC_2O_4), ferric hydroxide [$Fe(OH)_3$), and lanthanum potassium sulfate [$LaK(SO_4)_2$]. Americium (+4) is also coprecipitated with these reagents as well as with zirconium phosphate [$Zr_3(PO_4)_4$]. Americium(VI) is not coprecipitated with any of these reagents but with sodium uranyl acetate [$NaUO_2(C_2H_3O_2)_2$].

SOLVENT EXTRACTION. Organic solvents and chelating agents are available for separating americium from other radionuclides by selectively extracting either americium or the alternate radionuclide from aqueous solutions into an organic phase. Tributylphosphate (TBP) in kerosene or TTA in xylene removes most oxidation states of neptunium and plutonium from Am^{+3} in the presence of dilute nitric acid. The addition of sodium nitrate (6 M) tends to reverse the trend making americium more soluble in TBP than uranium, neptunium, or plutonium radionuclides. Bis(2-ethylhexyl) phosphoric acid (HDEHP) in toluene is highly effective in extracting Am^{+3} and is used in sample preparation for alpha spectroscopic analysis.

Plutonium in the +4 oxidation state can interfere with Am analysis. See Section 14.10.9.8 on plutonium for a discussion of how to separate americium from plutonium.

ION EXCHANGE. Separation of americium can be achieved by cation-exchange chromatography. Any of its oxidation states exchange with a cation resin in dilute acid solution, but the higher oxidation states are not important in cation-exchange separations because they are unstable toward reduction to the +3 state. Generally, Am^{+3} is the last tripositive ion among the actinides eluted from a cation-exchange matrix, although the order may not be maintained under all conditions. Many eluting agents are available for specific separations. Concentrated hydrochloric acid, for example, has been used for separating actinides such as americium from the lanthanides. Anion-exchange chromatography has been widely used for separating americium. Anionic complexes of Am^{+3} form at high chloride concentrations, providing a chemical form that is easily exchanged on an anion-exchange column. The column can be eluted using dilute hydrochloric acid or a dilute hydrochloric acid/ammonium thiocyanate solution. Anion-exchange separations of americium are also realized with columns prepared with concentrated nitric acid solutions. The sequential separation of the actinides is accomplished readily using anion-exchange chromatography. Americium, plutonium, neptunium, thorium, protactinium, curium, and uranium can all be separated by the proper application of select acid or salt solutions to the column.

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

Methods of Analysis

Americium-241 is detected and quantified by alpha or gamma spectrometry, or by gas proportional counting (GPC). Trace quantities of ^{241}Am are analyzed by GPC, after separation from interfering radionuclides by solvent extraction, coprecipitation, or ion-exchange chromatography. The isolated radionuclide is collected and mounted on a planchet or electroplated onto a platinum electrode for counting by alpha spectrometry. Americium-243 is added to the analytical solution as a tracer to measure chemical yield. Americium-241 may be determined directly (i.e., no radiochemical separation) in bulk soil samples by gamma spectroscopy.

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

14.10.9.2 Carbon

The chemistry of carbon compounds is too extensive to be summarized here. Fortunately, only one isotope of carbon, ^{14}C, is significant in analytical separation. This chapter will focus on the two principal radioisotopes of carbon that are in use: ^{11}C and ^{14}C.

Isotopes

Carbon-11 has a half-life of 20 minutes. It is used for medical diagnoses and is prepared by proton bombardment of a boron target in an accelerator. The ^{11}C in the target then may be incorporated as part of a tracer molecule that would be used for the diagnosis. This isotope is also formed in nuclear reactors by the two reactions, $^{11}B(p, n)\,^{11}C$ and $^{12}C(n, 2n)^{11}C$.

The chemical environment in the reactor coolant system is highly reducing (overpressure of hydrogen gas is used to minimize oxygen formation from radiolysis of water). Thus, the chemical form of the carbon is most likely $^{11}CH_4$. The radioisotope decays to ^{11}B by positron emission. It may be detected by liquid scintillation or gamma ray detection of the 511 keV annihilation peak. Its short half-life obviates the need for its environmental analysis.

Carbon-14 is also formed as a result of activation in reactor coolant systems of fission reactors from the following reaction: $^{17}O(n,\alpha)^{14}C$. As with ^{11}C, the chemical form will most likely be $^{14}CH_4$.

Occurrence

Carbon-14 is a naturally occurring radionuclide with a half-life of 5,720 years. It is formed as a result of $^{14}N(n, p)^{14}C$. The nitrogen atoms in the upper atmosphere are bombarded with high-energy neutrons emitted from the sun. The carbon becomes incorporated as part of a CO_2 molecule due to the presence of oxygen and many highly energetic particles and free radicals in the upper atmosphere. Carbon dioxide freely exchanges with all carbon using organisms in the environment. The living organism rapidly reaches a state of equilibrium with the environment because of the long half-life of the carbon. The rate of radioactive decay of naturally occurring ^{14}C is approximately 780 Bq (13 dpm) per gram of total carbon. However, once an organism dies, it ceases to exchange that carbon with the environment. Thus, the activity per gram of carbon would decrease with the characteristic half-life of ^{14}C (as long as the material is undisturbed). This is the basis for carbon dating of materials.

Solubility and Solution Chemistry

Organic compounds have a vast range of chemical and physical properties. Many of the ^{14}C containing materials one encounters will be insoluble in aqueous solution, but soluble in some organic solvents. Carbon is basically tetravalent in all compounds, and forms covalent bonds. Thus, when using separation techniques involving a carrier, such as CO_3^{-2}, it is necessary to ensure not only that the sample is dissolved, but that sufficient oxidative power has been employed to convert the analyte to the same chemical form. Carbon is also unique in that CO_2 is a common oxidation product of carbon and can easily escape from solution. The equilibria

$$CO_2 + H_2O \rightarrow HCO_3^{-1} + H^+$$

$$HCO_3^{-1} + H_2O \rightarrow CO_3^{-2} + H^+$$

demonstrate the significant effect that acid concentration can have on the loss of carbon, as CO_2, from solution. This must be taken into consideration whenever processing ^{14}C samples.

Dissolution

Many applications involve ^{14}C as tracers. As discussed later, no sample dissolution may be needed and analysis by one of the two analytical techniques may proceed directly.

Dissolution of samples containing ^{14}C where other isotopes are present involves the complete destruction of the organic matter in the sample, and simultaneously not allowing the volatilization of the carbon. This is most commonly achieved by permanganate oxidation in a basic solution. As seen in the equilibrium equations for carbon, in basic solution it is present as the CO_3^{-2} species, which is nonvolatile.

Samples also may be prepared by high temperature oxidation, in which the carbon is converted to CO_2. The exit gasses from the combustion process must be directed through a trap which will remove carbon dioxide. These include such materials as molecular sieve, barium chloride solutions or Ascarite® columns.

Methods of Analysis

Carbon-14 decays only by β^- emission. The $E_{\beta max}$ of this emission is 0.156 MeV. Although it is detectable by gas proportional counting, the only two methods of analysis commonly used for this isotope are liquid scintillation and mass spectroscopic analysis. The methods for liquid scintillation analyses are described in Chapter 15, *Quantification of Radionuclides*, and Kessler (1989).

14.10.9.3 Cesium

Cesium is the last member of the naturally occurring alkali metals in Group IA of the Periodic Table, with an atomic number of 55. Its radiochemistry is simplified because the Group IA metals form only +1 ions. Elemental cesium is a very soft, silver-white metallic solid in the pure state with a melting point of only 28.5 °C. It tarnishes quickly to a golden-yellow color when exposed to small amounts of air. With sufficient air, it ignites spontaneously. It is normally stored under xylente or toluene to prevent contact with air.

Isotopes

Cesium isotopes of mass number 112 to 148 have been identified. Cesium-133 is the only stable isotope. Cesium-134, ^{136}Cs and ^{137}Cs are the only isotopes of significance from an environmental perspective. They are formed from the nuclear fission process. Their half-lives are 2.06 years, 13.2 days, and 30.17 years, respectively. Cesium-135 also is formed as a result of the fission process. However, it is not a significant isotope, because it is a low-energy (0.21 MeV) beta-only emitter with a long half-life (2.2×10^6 years).

Occurrence

Cesium is widely distributed in the Earth's crust with other alkali metals. In granite and sedimentary rocks the concentration is less than 7 ppm. In seawater it is about 0.002 ppm, but in mineral springs the concentration may be greater than 9 mg/L. Cesium-137 is produced in nuclear fission and occurs in atmospheric debris from weapons tests and accidents. It is a very important component of radioactive fallout; and because of its moderately long half-life and high solubility, it is a major source of long-lived external gamma radiation from fallout. It accounts for 30 percent of the gamma activity of fission products stored for one year, 70 percent in two years, and 100 percent after five years.

Cesium metal's most recognized use is in the atomic clock that serves to define the second. Cesium has been considered as a fuel in ion-propulsion engines for deep space travel and as a heat-transfer medium for some applications. Cesium-137 has replaced ^{60}Co in the treatment of cancer and has been used in industrial radiography for the control of welds. Cesium-137 is also used commercially as a sealed source in liquid scintillation spectrometers. The 661 keV gamma ray it emits is used to create an electron (Compton effect) distribution, which allows the degree of sample quench to be determined.

Solubility of Compounds

Most cesium salts are very soluble in water and dilute acids. Among the salts of common anions, the notable exceptions are cesium perchlorate and periodate ($CsClO_4$ and $CsIO_4$). Several cesium compounds of large anions are insoluble. Examples include the following: silicotungstate [$Cs_8SiW_{12}O_{42}$], permanganate ($CsMnO_4$), chloroplatinate (Cs_2PtCl_6), tetraphenylborate [$CsB(C_6H_5)_4$], alum [$CsAl(SO_4)_2$], and cobaltnitrate complex [$Cs_3Co(NO_3)_6$].

Review of Properties

Cesium is the most active and electropositive of all the metals. It forms compounds with most inorganic and organic anions; it readily forms alums with all the trivalent cations that are found in alums. The metal readily ionizes, and in ammonia solutions it is a powerful reducing agent. When exposed to moist air, it tarnishes initially forming oxides and a nitride and then quickly melts or bursts into flame. With water the reaction is violent. Cesium reacts vigorously with halogens and oxygen, and it is exceptional among the alkali metals in that it can form stable polyhalides such as CsI_3. Reaction with oxygen forms a mixture of oxides: cesium oxide (Cs_2O), cesium peroxide (Cs_2O_2), and cesium superoxide (CsO_2). The toxicity of cesium compounds is generally not important unless combined with another toxic ion.

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

Solution Chemistry

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

COMPLEXATION. Cesium ions form very few complex ions in solution. The few that form are primarily with nitrogen-donor ligands or beta-diketones. Anhydrous beta-diketones are insoluble in water, but in the presence of additional coordinating agents, including water, they become soluble in hydrocarbons. One solvent-extraction procedure from aqueous solutions is based on chelation of cesium with TTA in hydrocarbon solvents. Cesium is sandwiched between crown ligands, associated with the oxygen atoms of the ether, in $[Cs_9(18\text{-}C\text{-}6)_{14}]^{+9}$.

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

ADSORPTION. When cesium is present in extremely low concentrations, even in the presence of 2 M acid, adsorption on the walls of glass and plastic containers leads to complications for the radioanalyst. Half the activity of cesium radionuclides, for example, can be lost from acid solutions stored for one month in these containers. Experiments indicate that addition of 1 µg cesium carrier per milliliter of solution is sufficient to stabilize acid solutions for six months.

Dissolution of Samples

Radiochemists generally dissolve cesium samples from irradiated nuclear fuel, activated cesium salts, natural water, organic material, agriculture material, and soils. Nuclear fuel samples are generally dissolved in HCl, HNO_3, HF, or a combination of these acids. Care should be taken to ensure that the sample is representative if ^{137}Cs has been used as a burn-up monitor. Precautions should also be taken with these samples to prevent loss of cesium because of leaching or incomplete sample dissolution. Most cesium salts dissolve readily in water and acid solutions. In water samples, the cesium might require concentration, preferably by ion exchange, or by precipitation or coprecipitation if interfering ions are present. Organic materials are either decomposed by HNO_3 or dry ashed, and the cesium is extracted with hot water or hot acid solution. Extraction and leaching procedure have been use to assess exchangeable or leachable cesium using ammonium acetate solutions or acid solutions, but soils are generally completely solubilized in HNO_3, HCl, HF, H_2SO_4, or a mixture of these acids in order to account for all the cesium in a soil sample.

Separation Methods

PRECIPITATION AND COPRECIPITATION. Cesium is separated and purified by several precipitation and coprecipitation methods using salts of large anions. Gravimetric procedures rely on precipitation to collect cesium for weighing, and several radiochemical techniques isolate cesium radionuclides for counting by precipitation or coprecipitation. Cesium can be precipitated, or coprecipitated in the presence of cesium carrier, by the chlorate, cobaltinitrate, platinate, and tetraphenylborate ions. Other alkali metals interfere and should be removed before a pure insoluble compound can be collected. Cesium can be isolated from other alkali metals by precipitation as the silicotungstate. The precipitate can be dissolved in 6 M sodium hydroxide, and cesium can be further processed by other separation procedures. The tetraphenylborate procedure first removes other interfering ions by a carbonate and hydroxide precipitation in the presence of iron, barium, lanthanum, and zirconium carriers. Cesium is subsequently precipitated by the addition of sodium tetraphenylborate to the acidified supernatant. Alum also precipitates cesium from water samples in the presence of macro quantities of the alkali metals. Trace quantities of cesium radionuclides are precipitated using stable cesium as a carrier.

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

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

Methods of Analysis

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

Gamma ray spectrometry allows detection of ^{134}Cs, ^{136}Cs, and ^{137}Cs down to very low levels. The gamma ray measured for ^{137}Cs (661 keV) actually is emitted from it progeny ^{137m}Ba. However, because the half-life of the barium isotope is so short (2.5 min) it is quickly equilibrated with its parent cesium isotope (i.e., secular equilibrium). Cesium-137 is used as part of a group of nuclides in a mixed radioactivity source for calibration of gamma ray spectrometers. It is also used in some liquid scintillation spectrophotometers to generate a Compton distribution to determine the quench.

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

14.10.9.4 Cobalt

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

Isotopes

Cobalt-59 is the only naturally occurring isotope of the element. The other twenty-two isotopes and their metastable states, ranging from mass numbers 50 to 67, are radioactive. Isotopes with mass numbers less than 59 decay by positron emission or electron capture. Isotopes with mass numbers greater than 59 decay by beta and gamma emission. Except for ^{60}Co, the most important radionuclide, their half-lives range from milliseconds to days. The principal isotopes of cobalt (with their half-lives) are ^{57}Co ($t_{½} \approx 272$ d), ^{58}Co ($t_{½} \approx 71$ d), and ^{60}Co ($t_{½} \approx 5.27$ y). Isotopes 57 and 58 can be determined by X-ray as well as gamma spectrometry. Isotope 60 is easily determined by gamma spectrometry.

Occurrence and Uses

The cobalt content of the crust of the Earth is about 30 ppm, but the element is widely distributed in nature, found in soils, water, plants and animals, meteorites, stars, and lunar rocks. Over 200 cobalt minerals are known. Commercially, the most important are the arsenides, oxides, and sulfides. Important commercial sources also include ores of iron, nickel, copper, silver, manganese, and zinc. Cobalt-60 is produced by neutron activation of stable ^{59}Co. Cobalt-56 and ^{57}Co are prepared by bombardment of iron or nickel with protons or deuterons. Cobalt-58 (formed by activation of nickel) is now the dominant isotope formed in nuclear power plants during a fuel cycle, because most power plants have replaced their cobalt-bearing alloys, such as stellite.

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

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

Little use if made of pure cobalt except as a source of radioactivity from ^{60}Co. The radionuclide is used in cancer radiotherapy, as a high-energy gamma source for the radiography of metallic objects and other solids, as a food irradiation source for sterilization, or as an injectable radionuclide for the measurement of flow rates in pipes. The half-life of ^{60}Co ($t_{½} \approx 5.2$ y), and its gamma emissions make it a principal contributor to potential dose effects in storage and transport of radioactive waste.

Solubility of Compounds

Most simple cobalt compounds contain Co^{+2}, but Co^{+2} and Co^{+3} display varied solubilities in water. To some extent, their solubilities depend on the oxidation state of the metal. For example, all the halides of Co^{+2} are soluble but the only stable halide of Co^{+3}, the fluoride, is insoluble. The sulfates of both oxidation states are soluble in water. The acetate of Co^{+2} is soluble, but that of Co^{+3} hydrolyses in water. The bromate, chlorate, and perchlorate of Co^{+2} are also soluble. Insoluble compounds include all the oxides of both oxidation states, Co^{+2} sulfide, cyanide, oxalate, chromate, and carbonate. The hydroxides are slightly soluble. Several thousand complex compounds of cobalt are known. Almost all are Co^{+3} complexes and many are soluble in water.

Review of Properties

Metallic cobalt is less reactive than iron and is unreactive with water or oxygen in air unless heated, although the finely divided metal is pyrophoric in air. On heating in air it forms the oxides, Co^{+2} oxide (CoO) below 200 °C and above 900 °C and Co^{+2}-Co^{+3} oxide (Co_3O_4) between the temperature extremes. It reacts with common mineral acids and slowly with hydrofluoric and phosphoric acids to form Co^{+2} salts and with sodium and ammonium hydroxides. On heating, it reacts with halogens and other nonmetals such as boron, carbon, phosphorus, arsenic, antimony, and sulfur.

Cobalt exists in all oxidation states from -1 to $+4$. The most common are the +2 and +3 oxidation states. The +1 state is found in a several complex compounds, primarily the nitrosyl and carbonyl complexes and certain organic complexes. The +4 state exist in some fluoride complexes. Co^{+2} is more stable in simple compounds and is not easily hydrolyzed. Few simple compounds are known for the +3 state, but cobalt is unique in the numerous stable complex compounds it forms.

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

Solution Chemistry

In aqueous solution and in the absence of complexing agents, Co^{+2} is the only stable oxidation state, existing in water as the pink-red hexaaquo complex ion, $Co(H_2O)_6^{+2}$. Simple cobalt ions in the +3 oxidation state decompose water in an oxidization-reduction process that generates Co^{+2}:

$$4\,Co^{+3} + 2\,H_2O \rightarrow 4\,Co^{+2} + O_2 + 4\,H^{+1}$$

Complexation of Co^{+3} decreases its oxidizing power and most complex ions of the +3 oxidation state are stable in solution.

COMPLEXATION. Several thousand complexes of cobalt have been prepared and extensively studied, including neutral structures and those containing complex cations or anions. The +2 oxidation state forms complexes with a coordination of four or six, and in aqueous solution, $[Co(H_2O)_6]^{+2}$ is in equilibrium with some $[Co(H_2O)_4]^{+2}$. In alkaline solution Co^{+2} precipitates as $Co(OH)_2$, but the ion is amphoteric; and in concentrated hydroxide solutions, the precipitate dissolves forming $[Co(OH)_4]^{-2}$. Many complexes of the form $[Co(X)_4]^{-1}$ exist with monodentate anionic ligands such as Cl^{-1}, Br^{-1}, I^{-1}, SCN^{-1}, N_3^{-1}, and OH^{-1}. Many aquo-halo complexes are known; they are various shades of red and blue. The aquo complex, $[Co(H_2O)_6]^{+2}$, is pink.

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

OXIDATION-REDUCTION BEHAVIOR. Most simple cobalt +3 compounds are unstable because the +3 state is a strong oxidizing agent. It is very unstable in aqueous media, rapidly reducing to the +2 state at room temperature. The aqueous ion of Co^{+2}, $[Co(H_2O)_6]^{+2}$, can be oxidized, however, to the +3 state either by electrolysis or by ozone (O_3) in cold perchloric acid ($HClO_4$); solutions at 0 °C have a half-life of about one week. Compounds of the Co^{+3} complex ions are formed by oxidizing the +2 ion in solution with oxygen or hydrogen peroxide (H_2O_2) in the presence of ligands. The Co^{+3} hexamine complex forms according to:

$$4\ CoX_2 + 4\ NH_4X + 20\ NH_3 + O_2 \rightleftharpoons 4\ [Co(NH_3)_6]X_3 + 2\ H_2O$$

HYDROLYSIS. The hydrolysis of the +2 oxidation state of cobalt is not significant in aqueous media below pH 7. At pH 7, hydrolysis of 0.001 M solution of the cation begins and is significant at a pH above 9. The hydrolysis of the +3 oxidation state is reminiscent of the hydrolysis of Fe^{+3}, but it is not as extensive. Hydrolysis of Co^{+3} is significant at pH 5. In contrast, the hydrolysis of Fe^{+3} becomes significant at a pH of about 3.

Dissolution of Samples

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

Separation Methods

PRECIPITATION AND COPRECIPITATION. Cobalt can be precipitated by hydrogen sulfide (H_2S), ammonium sulfide (NH_4S), basic acetate ($C_2H_3O_2^{-1}/HO^{-1}$), barium carbonate ($BaCO_3$), zinc oxide (ZnO), potassium hydroxide and bromine (KOH/Br_2), ether and hydrochloric acid [$(C_2H_5)_2O$ and HCl], and cupferron. Cobalt sulfide (CoS) is coprecipitated with stannic sulfide (SnS_2) when low-solubility sulfides are precipitated in mineral acids. Care should be taken to avoid coprecipitation of zinc sulfide (ZnS).

Cobalt can be separated from other metals by hydroxide precipitation using pH control to selectively precipitate metals such as chromium, zinc, uranium, aluminum, tin, iron (+3), zirconium, and titanium at low pH. Cobalt precipitates at pH 6.8, and magnesium, mercury, manganese, and silver at a pH greater than 7. Cobalt is not be separated from metals such as iron, aluminum, titanium, zirconium, thorium, copper, and nickel using ammonium hydroxide (NH_4OH) solutions (aqueous ammonia), because an appreciable amount of cobalt is retained by the hydroxide precipitates of these metals produced using this precipitating agent. Various precipitating agents can be used to remove interfering ions prior to precipitating cobalt: iron by precipitating with sodium phosphate (Na_3PO_4) or iron, aluminum, titanium, and zirconium with zinc oxide.

The separation of cobalt from interfering ions can be achieved by the quantitative precipitation of cobalt with excess potassium nitrite (KNO_2) to produce $K_3[Co(NO_2)_6]$ (caution: heating $K_3[Co(NO_2)_6]$ after standing for some time makes it unstable). Ignition can be used to collect the cobalt as its mixed oxide (Co_3O_4). Cobalt can also be precipitated with α-nitroso-β-napthol (1-nitroso-2-napthol) to separate it from interfering metals. Nickel can interfere with this precipitation, but can be removed with dimethylglyoxime. Precipitation of Co^{+2} as mercury tetracyanatocobaltate (+2) {$Hg[Co(SCN)_4]$} also is used, particularly for gravimetric analysis, and precipitation with pyridine in thiocyanate solution is a quick gravimetric product, $[Co(C_5H_5N)_4](SCN)_2$.

SOLVENT EXTRACTION. Various ions or chelates have been used in solvent extraction systems to isolate cobalt from other metals. Separation has been achieved by extracting either cobalt itself or, conversely, extracting contaminating ions into an organic solvent in the presence of hydrofluoric acid (HF), hydrochloric acid, and calcium chloride ($HCl/CaCl_2$), hydrobromic acid (HBr), hydroiodic acid (HI), or ammonium thiocyanate (NH_4SCN). For example, Co^{+2} has been separated from Ni^{+2} by extracting a hydrochloric acid solution containing calcium chloride with 2-octanol. The ion is not extracted by diethyl ether from hydrobromic acid solutions, but it is extracted from ammonium thiocyanate solutions by oxygen-containing organic solvents in the presence of Fe^{+3} by first masking the iron with citrate.

Several chelate compounds have been used to extract cobalt from aqueous solutions. Acetylacetone (acac) forms a chelate with Co^{+3}, but not Co^{+2}, that is soluble in chloroform at pH 6 to 9, permitting separation from several metals including nickel. Co^{+2} can be oxidized to Co^{+3} with hydrogen peroxide (H_2O_2) prior to extraction. The chelating agent α-nitroso-β-napthol has also been used in the separation of Co^{+3} by solvent extraction. Diphenylthiocarbazone (dithizone) has been used at pH 8 to extract cobalt into carbon tetrachloride and chloroform after metals that form dithizonates in acid solution (pH 3-4) have been removed. 8-quinolinol has been used in a similar manner at pH up to 10. Masking agents added to the system impede the extraction of iron, copper, and nickel.

ION-EXCHANGE CHROMATOGRAPHY. Anion-exchange resins have been used extensively to separate cobalt from other metals. The chloro-metal complexes, prepared and added to columns in molar hydrochloric acid solutions, are eluted at varying concentrations of hydrochloric acid. Trace amounts of ^{59}Fe, ^{60}Co, and ^{65}Zn and their respective carriers have been separated from neutron-irradiated biological tissue ash with a chloride system. Cobalt-60 has been eluted carrier-free from similar samples and columns prepared with hydrobromic acid. Cobalt and contaminated metals in nitric-acid systems behave in a manner similar to hydrochloric-acid systems. Co^{+2}-cyanide and cyanate complexes have been used to separate cobalt from nickel. The basic form of quaternary amine resins (the neutral amine form) has been used in the column chromatography of cobalt. Both chloride- and nitrate-ion systems have resulted in the association of cobalt as a complex containing chloride or nitrate ligands as well as the neutral (basic) nitrogen atom of the amine resin. Resins incorporating chelates in their matrix system have been used to isolate cobalt. 8-quinolinol resins are very effective in separating cobalt from copper.

ADSORPTION CHROMATOGRAPHY. Several inorganic adsorbents such as alumina, clays, and silica are used to separate cobalt. Complex ions of cobaltamines separate on alumina as well as Co^{+2} complexes of tartaric acid and dioxane. A complex of nitroso-*R*-salts are adsorbed onto an alumina column while other metals pass through the column. Cobalt is eluted with sulfuric acid. Cobalt dithizonates adsorb on alumina from carbon tetrachloride solutions. Cobalt is eluted with acetone. The separation of cobalt from iron and copper has been achieved on aluminum hydroxide [$Al(OH)_3$]. Clay materials—kaolinite, bentonite, and montmorillonite—separate Co^{+2} from Cu^{+2}. Cu^{+2} adsorbs and Co^{+2} elutes with water. Silica gel and activated silica have both been used as adsorbents in cobalt chromatography.

Organic adsorbents such as 8-hydroxyquinoline and dimethylglyoxime have been used in cobalt-adsorption chromatographic systems. Powdered 8-hydroxyquinoline separates Co^{+2} from other cations and anions, for example, and dimethylglyoxime separates cobalt from nickel. Cobalt-cyano complexes adsorb on activated charcoal, and cobalt is eluted from the column while the anionic complexes of metals such as iron, mercury, copper, and cadmium remain on the column.

Numerous paper chromatograph systems employing inorganic or chelating ligands in water or organic solvents are available to separate cobalt from other metals. In one system, carrier-free ^{60}Co and ^{59}Fe from an irradiated manganese target were separated with an acetone-hydrochloric solvent.

ELECTRODEPOSITION. Most electroanalytical methods for cobalt are preceded by isolating the cobalt from interfering ions by precipitation or ion exchange. The electrolyte is usually an ammonia solution that produces the hexamine complex of Co^{+2}, $Co(NH_3)_6^{+2}$ in solution. Reducing agents such as hydrazine sulfate are added to prevent anodic deposits of cobalt and the oxidation of the Co^{+2}-amine ion. Cobalt and nickel can be separated electrolytically by using an aqueous solution of pyridine with hydrazine to depolarize the platinum anode. The nickel is deposited first, and the voltage is increased to deposit cobalt.

Methods of Analysis

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

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

14.10.9.5 Iodine

Iodine is a nonmetal, the last naturally occurring member of the halogen series, with an atomic number of 53. In the elemental form it is a diatomic molecule, I_2, but it commonly exists in one of four nonzero oxidation states: -1 with metal ions or hydrogen; and +1, (V), and (VII) with other nonmetals, often oxygen. Numerous inorganic and organic compounds of iodine exist, exhibiting the multiple oxidation states and wide range of physical and chemical properties of the element and its compounds. Existence of multiple oxidation states and the relative ease of changing between the -1, 0, and (V) state allows readily available methods for separation and purification of radionuclides of iodine in radiochemical procedures.

Isotopes

There are 42 known isotopes of iodine, including seven metastable states. The mass numbers range from 108 to 142. The only stable isotope is naturally occurring ^{127}I. The half-lives of the radionuclides range from milliseconds to days with the single exception of long-lived ^{129}I ($t_{1/2} \approx 1.57\times10^7$ y). Iodine radionuclides with lower mass numbers decay primarily by electron capture. The high mass numbers are, for the most part, beta emitters. The significant radionuclides are ^{123}I

($t_{1/2} \approx$ 13.2 h), ^{125}I ($t_{1/2} \approx$ 60.1 d, electron capture), ^{129}I (β), and ^{131}I ($t_{1/2} \approx$8 d, β).

Occurrence and Uses

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

Isotopes of iodine of mass ≥ 128 may all be formed as a result of fission of uranium and plutonium. Nuclear reactors and bomb tests are the most significant sources of these radioisotopes with the exception of ^{131}I. That isotope is routinely produced for use in medical imaging and diagnosis. The isotopes released from the other sources represent a short-term environmental health hazard should there be an abnormal release from a reactor or testing of bombs.

This was the case in 1979 and 1986 when the reactor incidents at Three Mile Island and Chernobyl caused releases of radioiodines. During the former event, a ban on milk distribution in the downwind corridor was enforced as a purely preventative measure. In the latter case, significant releases of iodines and other isotopes caused more drastic, long term measures for food quarantine.

Deposits on the surface of plants could provide a quick source of exposure if consumed directly from fruits and vegetables or indirectly from cow's milk. It would readily accumulate in the thyroid gland, causing a short-term exposure of concern. It represent the greatest short-term exposure after a nuclear detonation and has been released in power plant accidents. Iodine-129, with of a half-life of more than 15 million years, represent a long-term environmental hazard. In addition to its long half-life, the environmental forms of iodine in the environment are highly soluble in groundwater and are poorly sorbed by soil components. It is not absorbed at all by granite, and studies at a salt repository indicate that ^{129}I would be only one of few radionuclides that would reach the surface before it decayed. Therefore, research on the fate of ^{129}I that might be released suggests that the radionuclide would be highly disseminated in the ecosystem.

Iodine-131 is analyzed routinely in milk, soil and water. Iodine-129 is a low energy beta and gamma emitter, which has a very long half-life ($t_{½} \approx 1.47 \times 10^7$ y). The most significant concern for this isotope is in radioactive waste, and its potential for migration due to the chemistry of iodine in the environment. Iodine-131 is produced for medical purposes by neutron reaction as follows: $^{130}\text{Te}(n,\gamma)^{131}\text{Te} \rightarrow$ beta decay $\rightarrow$ ^{131}I ($t_{½} \approx 8$ d).

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

Solubility of Compounds

Molecular iodine is only very slightly soluble in water (0.33 g/L), but it is soluble in solutions of iodide ion, forming I_3^{-1}. It is appreciably soluble in organic solvents. Carbon tetrachloride (CCl_4) or chloroform ($CHCl_3$) are commonly used to extract iodine from aqueous solutions after alternate forms of the element, typically I^{-1} and IO_3^{-1}, are converted to I_2. The solutions have a violet color in organic solvents, and iodine dimerizes to some extent in these solutions:

$$2\, I_2 \rightleftharpoons I_4$$

Numerous compounds of iodine are soluble in water. All metallic iodides are soluble in water except those of silver, mercury, lead, cupurous ion, thallium, and palladium. Antimony, bismuth, and tin iodides require a small amount of acid to keep them in solution. Most of the iodates and periodates are insoluble. The iodates of sodium, potassium, rubidium, and the ammonium ion are soluble in water. Those of cesium, cobaltous ion, magnesium, strontium, and barium are slightly soluble in water but soluble in hot water. Most other metallic iodates are insoluble.

Review of Properties

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

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

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

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

The radionuclides of iodine are radiotoxic, primarily because of their concentration in the thyroid gland. Toxicity of ^{129}I, if released, is a concern because of its extremely long half-life. Iodine-131, with a half-life of eight days, is a short-term concern. The whole-body effective biological half-lives of ^{129}I and ^{131}I are 140 d and 7.6 d, respectively.

Solution Chemistry

OXIDATION-REDUCTION BEHAVIOR. Iodine can exist in multiple oxidation states in solution, but the radiochemist can control the states by selection of appropriate oxidizing and reducing agents. In acid and alkaline solutions, the common forms of iodine are: I^{-1}, I_2, and IO_3^{-1}. Hypoiodous acid (HIO) and the hypoiodite ion (IO^{-1}) can form in solution, but they rapidly disproportionate:

$$5\ HIO \rightleftharpoons 2\ I_2 + IO_3^{-1} + H^{+1} + 2\ H_2O$$

$$3\ IO^{-1} \rightleftharpoons 2\ I^{-1} + IO_3^{-1}$$

Iodine itself is not a powerful oxidizing agent, less than that of the other halogens (F_2, Cl_2, and Br_2), but its action is generally rapid. Several oxidizing and reducing agents are used to convert iodine into desired oxidation states during radiochemical procedures. These agents are used to promote radiochemical equilibrium between the analyte and the carrier or tracer or to produce a specific oxidation state before separation: I_2 before extraction in an organic solvent or I^{-1} before precipitation, as examples. Table 14.18 presents oxidizing and reducing agents commonly used in radiochemical procedures:

Table 14.18 — Common radiochemical oxidizing and reducing agents for iodine

Redox Process	**Redox Reagent**
$I^{-1} \rightarrow I_2$	HNO_2 ($NaNO_2$ in acid)
$I^{-1} \rightarrow IO_3^{-1}$	MnO_2 in acid
$I_2 \rightarrow I^-$	6 M HNO_3 $NaHSO_3$ and $NaHSO_4$ (in acid) Na_2SO_3 and $Na_2S_2O_3$ $Fe_2(SO_4)_3$ (in acid) SO_2 gas $NaHSO_3$ and $(NH_4)_2SO_3$
$I^{-1} \rightarrow IO_4^{-1}$	$KMnO_4$ 50% CrO_3 in 18N H_2SO_4
$I^{-1} \rightarrow IO_4^{-1}$	NaClO in base
$IO_4^{-1} \rightarrow I_2$	$NH_2OH{\cdot}HCl$
$IO_3^{-1} \rightarrow I_2$	$NH_2OH{\cdot}HCl$ $H_2C_2O_4$ in 18N H_2SO_4
$IO_4^{-1} \rightarrow I^{-1}$	$NaHSO_3$ in acid

Radiochemical exchange between I_2 and I^{-1} in solution is complete within time of mixing and before separation. In contrast, exchange between I_2 and IO_3^{-1} or IO_4^{-1} in acid solution and between IO_3^{-1} and IO_4^{-1} in acid or alkaline solution is slow. For radiochemical analysis of iodine, experimental evidence indicates that the complete and rapid exchange of radioiodine with carrier iodine can be accomplished by the addition of the latter as I^{-1} and subsequent oxidation to IO_4^{-1} by NaClO in alkaline solution, addition of IO_4^{-1} and reduction to I^{-1} with $NaHSO_3$, or addition of one followed by redox reactions first to one oxidation state and then back to the original state.

COMPLEXATION. As a nonmetal, iodine is generally not the central atom of a complex, but it can act as a ligand to form complexes such as SiI_6^{-2} and CoI_6^{-3}. An important characteristic of molecular iodine is its ability to combine with the iodide ion to form polyiodide anions. The brown triioide is the most stable:

$$I_2 + I^{-1} \rightleftharpoons I_3^{-1}$$

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

HYDROLYSIS. Iodine hydrolyzes in water through a disproportionation reaction:

$$I_2 + H_2O \rightleftharpoons H^{+1} + I^{-1} + HIO$$

Because of the low solubility of iodine in water and the small equilibrium constant ($k=2.0\times10^{-13}$), hydrolysis produces negligible amounts of the products (6.4×10^{-6} M) even when the solution is saturated with iodine. Disproportionation of HIO produces a corresponding minute quantity of IO_3^{-1} (see the reaction above). In contrast, in alkaline solution, I_2 produces I^{-1} and IO^{-1}:

$$I_2 + 2\ OH^{-1} \rightleftharpoons I^{-1} + IO^{-1} + H_2O$$

The equilibrium constant favors the products ($K = 30$), but the actual composition of the solution is complicated by the disproportionation of IO^{-1} (illustrated above), giving I^{-1} and IO_3^{-1}. The equilibrium constant for the reaction of IO^{-1} with hydroxide ion is very large (10^{20}), and the rate of the reaction is very fast at all temperatures. Therefore, the actual products obtained by dissolving iodine in an alkaline solution are indeed I^{-1} and IO_3^{-1}, quantitatively, and IO^{-1} does not exist in the solution.

Dissolution of Samples

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

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

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

Separation Methods

PRECIPITATION. The availability of stable iodine as a carrier and the relative ease of producing the iodide ion make precipitation a simple method of concentrating and recovering iodine radionuclides. The two common precipitating agents are silver (Ag^{+1}) and palladium (Pd^{+2}) cations, which form silver iodide (AgI) and palladium iodide (PdI_2), respectively. Silver iodide can be solubilized with a 30 percent solution of potassium iodide. Palladium precipitates iodide in the presence of chloride and bromide, allowing the separation of iodide from these halides.

The precipitating agent should be free of Pd^{+4}, which will precipitate chloride. If Pd^{+2} iodide is dried, precaution should be taken as the solid slowly looses iodine if heated at 100 °C. Iodate can be precipitated as silver iodate, and periodate as lead periodate.

SOLVENT EXTRACTION. One solvent extraction method is commonly used to isolate iodine. After preliminary oxidation-reduction steps to insure equilibrium of all iodine in solution, molecular iodine (I_2) is extracted from aqueous solutions by a nonpolar solvent, usually carbon tetrachloride or chloroform. It is not uncommon to add trace quantities of the oxidizing or reducing agent to the extraction solution to ensure and maintain all iodine in the molecular form. Hydroxylamine is added, for example, if iodate is the immediate precursor of iodine before extraction.

ION-EXCHANGE CHROMATOGRAPHY. Both cation and anion exchange procedures are used to separate iodine from contaminants. Cation-exchange chromatography has been used to remove interfering cations. To remove ^{137}Cs activity, an iodine sample in the iodide form is exchanged on a cation resin and eluted with ammonium sulfite [$(NH_4)_2SO_3$] to ensure maintenance of the iodide form. Cesium cations remain on the resin. Bulk resin also is used, and iodide is washed free of the resin also with sodium hypochlorite (NaClO) as the oxidizing agent. Anion resins provide for the exchange of the iodide ion. The halides have been separated from each other on an anion-exchange column prepared in the nitrate form by eluting with 1 M sodium nitrate. Iodide can also be separated from contaminants by addition to an anion exchanger and elution as periodate with sodium hypochlorite. The larger periodate anion is not as strongly attracted to the resin as the iodide ion. Iodine-131 separation, collection, and analysis is performed by absorbing the radionuclide on an anion-exchange resin and gamma counting it on the sealed column after eluting the contaminants.

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

Methods of Analysis

Macroquantities of iodine can be determined gravimetrically by precipitation as silver iodide, palladium iodide, or cuprous iodide. The last two substances are often used to determine the chemical yield in radiochemical analyses. Microquantities of ^{129}I and ^{131}I are coprecipitated with palladium iodide or cuprous iodide using stable iodide as a carrier and counted for quantification. Iodine-129 usually is beta-counted in a liquid-scintillation system, but it also can be determined by gamma-ray spectrometry. Iodine-129 can undergo neutron activation and then be measured by gamma-ray spectrometry from the ^{130}I ($t_{½}$ ≈ 12.4 h) produced by the neutron-capture reaction. The method uses conventional iodine valence adjustments and solvent extraction to isolate the Iodine fraction. Chemically separated ^{129}I is isolated on an anion exchange resin before being loaded for irradiation. A lower limit of detection (0.03 ng) can be achieved with a neutron flux of 5×10^{14} n/cm^2·s for 100 seconds. Iodine-129 also can be determined directly by mass spectrometry. The measurement limit by this technique is approximately 2 femtograms. Special counting techniques, such as beta-gamma coincidence, have also been applied to the analysis of ^{129}I. Iodine-131 is determined by gamma-ray emission. Mass spectrometry has been used for measurement of ^{125}I and ^{129}I.

> Compiled from: Adams, 1995; APHA, 1998; Armstrong et al., 1961; Bailar et al., 1984; Bate and Stokely, 1982; Choppin et al., 1995; Considine and Considine, 1983; Cotton and Wilkinson, 1988; DOE, 1990 and 1997, 1997; EPA, 1973; EPA, 1980; Ehmann and Vance, 1991; Greenwood and Earnshaw, 1984; Haissinsky and Adloff, 1965; Kleinberg and Cowan, 1960; Latimer, 1952; Lindsay, 1988; McCurdy et al., 1980; Strebin et al., 1988.

14.10.9.6 Neptunium

Neptunium, atomic number 93, is a metal and a member of the actinide series. The relatively short half-lives of the neptunium isotopes obviate naturally occurring neptunium from being detected in environmental samples (except in some rare instances). Thus, all detected isotopes are produced artificially, principally by neutron bombardment of uranium. Neptunium has six possible oxidation states: +2, +3, +4, (V), (VI), and (VII). The most stable ionic form of neptunium is the NpO_2^{+1} ion. The ionic states of neptunium are similar to that of manganese, however the chemistry is most closely associated with uranium and plutonium.

Isotopes

There are 17 isotopes of neptunium, which include three metastable states. The mass range of neptunium isotopes is from 226 to 242. All isotopes are radioactive, and the longest-lived isotope, ^{237}Np, has a half-life of 2.1×10^6 years and decays by alpha emission (principal decay mode) or spontaneous fission (very low probability of occurrence). The most common mode of decay for the other neptunium isotopes is by β-particle emission or electron capture.

Neptunium is formed in nuclear reactors from two separate neutron-capture reactions with uranium. Thus the largest quantity of neptunium isotopes are associated with spent nuclear fuel. In fuel reprocessing, the focus is on the recovery of uranium and plutonium isotopes. Thus the neptunium isotopes are part of the waste stream from that process.

The short-lived ^{239}Np can be used as a tracer when separated from its parent ^{243}Am. With the half-life of the americium at 7,370 years, and that of the neptunium is only 2.3 days, tracer quantities can be successfully removed every 6–10 days from an americium source.

Occurrences and Uses

Neptunium was the first of the actinides to be produced synthetically (in 1940). Neptunium-239 ($t_{½} \approx 25$ min) resulted from neutron bombardment of natural uranium.

Neptunium-237 is formed as a result of successive neutron capture on a ^{235}U nucleus to form ^{237}U. This uranium isotope has a reasonably short half-life (6.75 d). After a ^{235}U target has been irradiated with neutrons, most of the ^{237}U activity will have decayed to ^{237}Np after about 30 days (no radiochemical equilibrium; see Attachment 14A, "Radioactive Decay and Equilibrium"). At that time, the ^{237}Np may be "milked" from the source.

Neptunium-237 ($t_{½} \approx 2.1 \times 10^6$ y), is irradiated with neutrons to form ^{238}Np, which decays to ^{238}Pu. Plutonium-238 is used in space vehicles as a power source because of its superior energy characteristics. Neptunium-237 can be used in neutron detection equipment because it has a significant (n,γ) capture cross-section. The ^{238}Np produced has a half-life of 2.1 days with easily determinable beta or gamma emissions.

Solubility of Compounds

Neptunium solubility is strongly dependent upon oxidation state. The +3 and +4 states form very insoluble fluorides, while the (V) and (VI) states are soluble. This property is an effective means of separation of neptunium from uranium. Neptunium (+4) may be carried on zirconium phosphate precipitate, indicating its insolubility as a phosphate only in that oxidation state.

Neptunium forms two oxides, NpO_2 and Np_3O_8, both of which are soluble in concentrated hydrochloric, perchloric and nitric acids. The most soluble of the neptunium compounds are $Np(SO_4)_2$, $Np(C_2O_4)_2$, $Np(NO_3)_5$, $Np(IO_3)_4$, and $(NH_4)_2Np_2O_7$. Neptunium (+3) compounds are easily oxidized to Np^{+4} when exposed to air.

Review of Properties

Neptunium is a silvery, white metal, which is rapidly oxidized in air to the NpO_2 compound. NpF_3 is formed by the action of hydrogen and HF on NpO_2. NpF_4 is formed by the action of oxygen and HF on NpF_3. These reactions, and similar ones for the other halides take place at ~500 °C. All the halides are volatile above 450 °C, with the hexafluoride boiling at 55 °C. All the halides undergo hydrolysis in water to form the oxo-complex or ions.

Neptunium is found in the environment at very low concentrations due to the short half-lives of its isotopes and the few reactions through which ^{237}Np, its long-lived isotope, can be formed. The principal nuclear reactions are identified here:

$$^{238}U(n, 2n)^{237}U \rightarrow {}^{237}Np + \beta^-$$

$$^{235}U(n,\gamma) \rightarrow {}^{236}U(n,\gamma) \rightarrow {}^{237}U \rightarrow {}^{237}Np + \beta^-$$

Solution Chemistry

Neptunium most closely resembles uranium in its solution chemistry, although it has many differences that allow it to be easily separated. The +4 and (V) oxidation states are the two most commonly encountered in chemical and environmental analysis of neptunium.

COMPLEXATION. Neptunium forms complexes with fluorides, oxalates, phosphates, sulfates, and acetates in the +4 oxidation state at the macro level. However, for chemical separation of neptunium in concentrations found in environmental samples, the sulfate or the fluoride of the +4 oxidation state can be co-precipitated with $BaSO_4$ or LaF_3, respectively.

Neptunium (+4) also forms strong complexes in HCl and HNO_3 with the chloride and nitrate anions. These complexes appear to have similar complexation constants and charge densities as those of U(VI) and Pu(VI) in the same media. Neptunium(V) forms weak complexes with oxalate ions. Complexation in basic media with potassium phosphotungstate or lithium hydroxide has been shown to be a useful method for oxidation-reduction potential measurements as the individual oxidation states are stabilized significantly.

OXIDATION-REDUCTION. The most stable oxidation state of neptunium in aqueous solution is (V). Oxidation in basic solution to (VI) can be achieved with MnO_4^-, or BrO_3^-. Like manganese, neptunium can form the (VII) state. This can be achieved in basic solution with nitrous oxide, persulfate, or ozone.

Solutions of Np(V) can undergo disproportionation to yield the (VI) and +4 oxidation states. This reaction has a small equilibrium constant. However, in sulfuric acid media this may be accelerated a thousand fold, because sulfates complex with the Np^{+4} ion, driving the disproportionation reaction towards completion.

Dissolution of Samples

The dissolution of samples containing neptunium must be rigorous in ensuring complete dissolution, because no stable isotopes of neptunium exist to act as carriers. High temperature furnace oxidation of soil, vegetable, and fecal samples will ensure that the neptunium will be in the (VI) oxidation state. The resultant ash can be dissolved using lithium metaborate or perchloric acid. At that point it may be selectively reduced to either the (V) or +4 oxidation state, depending upon the other analytes from which it must be separated.

Separation Methods

PRECIPITATION AND COPRECIPITATION. The only samples that will have a significant amount of neptunium will be high-level wastes (HLW) resulting from spent fuel. Thus, for other sample analyses, the methods of precipitation of neptunium usually involve the use of a co-precipitant. In this respect, neptunium acts just like uranium. The +4 oxidation state is the one that will co-precipitate with LaF_3. If Np(V) or (VI) are formed, they will not precipitate with fluoride but stay in solution. This is analogous to the chemistry of the U^{+4} and U(VI) ions in solution.

Neptunium, like the other actinides, will flocculate with a general precipitating reagent such as iron hydroxide or titanium hydroxide.

SOLVENT EXTRACTION. Neptunium can be extracted into organic solvents such as methyl isobutyl ketone (MIBK), TBP, xylene and dibutoxytetraethylene glycol. The +4, (V), and (VI) oxidation states are extracted using these solvents under a variety of conditions. In all cases, care must be taken to eliminate or mask any fluorides, oxalates, or sulfates that are present, because they will have a significant effect on the extraction efficiency. The extraction process is aided by complex-forming compounds such as TTA, TIOA, trioctylphosphine oxide (TOPO), or tributylamine (TBA). Several different methods have been developed that use combinations of these chelates as well. In these instances a synergistic effect has been noted.

ION-EXCHANGE CHROMATOGRAPHY. The four principal neptunium oxidation states are soluble in dilute to concentrated HCl, $HClO_4$, HNO_3, and H_2SO_4. Although neptunium forms complexes with these ions in solution the exchange constant for a cation exchange resin is much greater, and the Np ions are readily removed for the aqueous system. The elution pattern of the oxidation states is, as with the other transuranics, lowest to highest ionic charge density. Thus the most strongly retained is the +4:

$$NpO_2^+ < NpO_2^{2+} < Np^{3+} < Np^{4+}.$$

Neptunium can be separated effectively from uranium and plutonium using an anion exchange method. The plutonium and neptunium are reduced to the +4 state with uranium as (VI) in HCl. The uranium elutes, while the neptunium and plutonium are retained. The plutonium may then be reduced to the +3 state using iodide or hydrazine, and will be eluted off the resin in the HCl solution.

More recently, resin loaded with liquid extractants has been used very successfully to separate the actinides. Neptunium can be separated selectively from plutonium and uranium using a TEVA® column, after the neptunium has been reduced to the +4 state using ferrous sulfamate. This process has been shown to be successful for water, urine, soil, and fecal samples.

Methods of Analysis

Neptunium-237 is the radioisotope most commonly used as a tracer for neptunium recovery. The principal means of detection of this isotope is alpha spectrometry following a NdF_3 or LaF_3 coprecipitation step. The 4.78 MeV alpha peak is easily resolved from other alpha emitters (notably plutonium) whose chemistry is analogous to that of neptunium. The ^{239}Np radioisotope could also be used as a tracer. It could be isolated from the parent ^{243}Am source, whose characteristic gamma-ray of 106 keV is used for quantitation. The other neptunium isotopes are most easily determined after separation and appropriate sample mounting using gas flow proportional counting.

Compiled from: Horwitz et al., 1995; Morss and Fuger, 1992; Sill and Bohrer, 2000.

14.10.9.7 Nickel

Isotopes

Twenty-four isotopes of nickel exist from mass number 51 to 74. It has five stable isotopes, and the most significant of its radioisotopes are ^{63}Ni ($t_{½} \approx$ 100 y) and ^{59}Ni ($t_{½} \approx 7.6 \times 10^4$ y). All other isotopes have half-lives of 5 days or less.

Occurrence

Nickel is found in nature as one of two principal ores, pentlandite or pyrrhotite. It is also a significant constituent of meteorites. It is a silvery white metal used in the production of Invar, Hastalloy, Monel, Inconel and stainless steels. Its other principal use is in coins. Corrosion resistant alloys containing nickel are used in the fabrication of reactor components. During the life cycle of the reactor, the nickel is converted to the two long-lived radionuclides through the following reactions: ^{58}Ni(n,γ)^{59}Ni and ^{62}Ni(n,γ)^{63}Ni.

The *Code of Federal Regulations* (Title 10, Part 61) identifies these isotopes as having specific limits "in activated metal,"because the material must be physically sampled and dissolved in order to assess the level of contamination of these isotopes in the metal.

Nickel-63 is a key component in the electron-capture detector of gas chromatographic systems. This technique is used particularly for organic compounds containing chlorine and phosphorus. Nickel-63 decays by emission of a low-energy beta ($E_{\beta\max}$ = 0.066 MeV), which establishes a baseline current in the detector system. When a compound containing phosphorus or chlorine passes the source, these elements can "capture an electron." The response to this event is an electrical current less than the baseline current, which is converted into a response used to quantify the amount of material.

Solubility of Compounds

The soluble salts of nickel are chlorides, fluorides, sulfates, nitrates, perchlorates, and iodides. Nickel sulfide is very insoluble and will dissolve initially from solutions at low pH. However, upon exposure to air, such solutions will form the very insoluble compound Ni(OH)S. Nickel hydroxide is also insoluble ($K_{sp} = 2 \times 10^{-16}$) and forms a very gelatinous precipitate, which can scavenge other radionuclides. Thus, avoiding the formation of this compound is very important. Solutions of neutral pH, where nickel is suspected of being a component, should be treated with ammonia to maintain the solubility of this metal ion.

Review of Properties

Nickel metal is highly resistant to air or water oxidation. It exists in the +2 oxidation state under normal conditions. It can be oxidized to the +3 oxidation state, to NiO(OH), by treatment of Ni^{+2} with aqueous bromine in potassium hydroxide. It can exist as a +4 ion in compounds such as NiO_2 (used in NiCad batteries), by oxidation with strong oxidants such as peroxydisulfate. In the +4 oxidation state nickel is a very strong oxidant and will react with water in aqueous solutions.

Nickel metal has been used in the radiochemistry laboratory as an electrode for the galvanic plating of polonium from hydrochloric acid solutions (see Section 14.10.9.17). In these instances, the polonium is being removed as interference in the alpha analysis of uranium or plutonium.

Solution Chemistry

Acid solutions of macroscopic quantities of nickel are emerald green. This is due to the formation of the hexaaquonickel complex, which is very stable.

OXIDATION. Nickel metal will readily dissolve in most mineral acids. The exception is in concentrated nitric acid, where the metal forms a passive oxide layer resistant to normal oxidation. Under normal laboratory conditions it will only form the +2 ion.

An usual property of nickel metal is that it forms a volatile carbonyl complex (boiling point 50 °C) when treated with carbon monoxide gas at low temperatures. This carbonyl compound decomposes to nickel metal at 200 °C. Thus, for samples with a high organic content that may be placed in a furnace for combustion, a high flow of air or oxygen should be assured if nickel is going to be analyzed for in the residue.

COMPLEXATION. Nickel forms strong complexes with nitrogen containing compounds such as ammonia, ethylene diamine, EDTA, and diethylenetriamine. The complex with ammonia forms a deep blue color distinct from the green color of the normal aqueous ion. The nickel ammonia complex has a large formation constant and is very stable in the pH range 7–10. This particular property of nickel is used to separate it from other metals and transuranics that may precipitate in ammonaical solution at this pH.

Nickel forms a weak complex with chloride ion as the tetrachloronicollate (+2) anion. This forms the basis of its separation from other first row transition elements iron and cobalt. The complex, $Ni^{+2} + 4Cl^{-} \rightarrow NiCl_4^{-2}$, is only stable in solutions greater than 10 M in HCl (see ion exchange section). Nickel forms complexes with the chelating agent diphenylthiocarbazone, which can be extracted into organic solvents to form the basis of a separation form other transition metals.

Dissolution of Samples

Samples containing nickel radionuclides are most likely to be corrosion products, pure metals that have been irradiated, or environmental water or soil samples. Dissolution of nickel and its compounds from these matrices can be achieved using any combination of concentrated mineral acids.

Separation Methods

PRECIPITATION. The classical method of nickel determination by gravimetric analysis is through precipitation with dimethylglyoxime (DMG). This material is very specific to nickel and forms a crystalline precipitate that is easily dried and weighed. The precipitation is carried out at pH 2-3, in the absence of other macroscopic metal contaminants. Aluminum, iron, and chromium can interfere but can be sequestered at pH 7–10 in ammoniacal solution with added citrate or tartrate. The Ni-DMG precipitate may be dried, weighed, and the mass used as the determination for yield of added nickel carrier.

SOLVENT EXTRACTION. Among the many solvent extraction methods for nickel, the following compounds are notably efficient: Cupferron, acetylacetone, TTA, dibenzoylmethane, and 8-hydroxyquinoline. The extractions almost uniformly are most effective at pH 5–10. Unfortunately, in each of these separation techniques, the most effective solvents are chloroform, benzene, or carbon tetrachloride, all of which have been phased out as analytical aids in separation analysis.

ION EXCHANGE. Nickel can be separated from other transition metals on an anion exchange column by dissolution of the sample in 12 M HCl. After the sample is loaded onto the column, lowering the HCl concentration to 10 M will elute the nickel.

Nickel also can be separated from cobalt in oxalate media using a cation exchange resin. The cobalt forms an anionic complex with the oxalate while the nickel does not. The cobalt passes through the resin and the nickel is retained.

Methods of Analysis

The ^{59}Ni and ^{63}Ni isotopes do not emit gamma radiation. Liquid scintillation or proportional counting after radiochemical separation can determine both isotopes. Nickel-59, as a very thin test source, also can be determined using a low energy gamma/X-ray detector. It decays by electron capture, and yields a characteristic X-ray of 6.93 keV. In a ^{63}Ni analysis, if ^{59}Ni is present in the test source, a correction for the liquid scintillation yield of the ^{59}Ni will be necessary. Chemical yield is determined by using a stable carrier and gravimetric analysis or spectrophotometric techniques.

> Compiled from: Cotton and Wilkinson, 1966; Freiser, 1983; Kraus and Nelson, 1958; Minczewski et al., 1982.

14.10.9.8 Plutonium

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

Isotopes

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

Occurrence and Uses

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

Plutonium is produced in nuclear reactors from ^{238}U that absorbs neutrons emitted by the fission of ^{235}U, which is a naturally occurring uranium isotope found with ^{238}U. Uranium-239 is formed and emits a beta particle to form ^{239}Np that decays by beta emission to form ^{239}Pu. Once started, the process is spontaneous until the uranium fuel rods become a specific uranium-plutonium mixture. The rods are dissolved in acid, and plutonium is separated primarily by solvent extraction, finally producing a concentrated plutonium solution. Pure plutonium metal can be prepared by precipitating plutonium peroxide or oxalate, igniting the precipitate to PuO_2, converting the oxide to PuF_3, and reducing Pu^{+3} to the metal in an ignited mixture containing metallic calcium.

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

Solubility of Compounds

General solubility characteristics include the insolubility of the hydroxides, fluorides, iodates, phosphates, carbonates, and oxalates of Pu^{+3} and Pu^{+4}. Some of these can be dissolved in acid solution, however. The corresponding compounds of PuO_2^{+1} and PuO_2^{+2} are soluble, with the exception of the hydroxides. The binary compounds represented by the carbides, silicides, sulfides, and selenides are of particular interest because of their refractory nature. One of the complicating factors of plutonium chemistry is the formation of a polymeric material by hydrolysis in dilute acid or neutral solutions. The polymeric material can be a complicating factor in radiochemical procedures and be quite unyielding in attempts to destroy it.

Review of Properties

Plutonium metal has some unique physical properties: a large piece is warm to the touch because of the energy produced by alpha decay, and it exists in six allotropic forms below its melting point at atmospheric pressure. Each form has unusual thermal expansion characteristics that prevents the use of unalloyed plutonium metal as a reactor fuel. The delta phase, however, can be stabilized by the addition of aluminum or gallium and be used in reactors. Chemically, plutonium can exist in five oxidation states: +3, +4, (V), (VI), and (VII). The first four states can be observed in solution, and solid compounds of all five states have been prepared. The metal is a silver-grey solid that tarnishes in air to form a yellow oxide coating. It is chemically reactive combining directly with the halogens, carbon, nitrogen, and silicon.

Plutonium is a very toxic substance. Outside the body, however, it does not present a significant radiological hazard, because it emits only alpha, low-energy beta, gamma, or neutron radiation. Ingested plutonium is not readily absorbed into the body, but passes through the digestive tract and expelled before it can cause significant harm. Inhaled plutonium presents a significant danger. Particularly, inhalation of particles smaller than one micron would be a serious threat due to the alpha-emitting radionuclide being in direct contact with lung tissue. Plutonium would also be very dangerous if it were to enter the blood stream through an open wound, because it would concentrate in the liver and bones, leading to damage to the bone marrow and subsequent related problems. For these reasons, plutonium is handled in gloveboxes with associated precautions taken to protect the worker from direct contact with the material. When working with plutonium in any form, precautions should also be taken to prevent the accumulation of quantities of fissionable plutonium that would achieve a critical mass, particularly in solution where it is more likely to become critical than solid plutonium.

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

Plutonium formed as a result of atmospheric tests is most likely to be in the form of a fine particulate oxide. If as in the case of a low altitude or underground test, there is a soil component, the plutonium will be fused with siliceous minerals. The behavior of the soluble form of plutonium would be similar to that released from fuel reprocessing plants and from nuclear waste sites. Like the insoluble oxide, most of the soluble form is found in sediments and soils, but a small percentage is associated with suspended particles in water. Both the soluble form of plutonium and the form suspended on particulate matter are responsible for plutonium transportation in the environment. Plutonium in soil is found where the humic acid content is high. In non-humic, carbonate-rich soils, plutonium migrates downward. Migration in the former soil is slow ($\leq$0.1 cm/y) and in the latter it is relatively fast (1–10 cm/y). In subsurface oxic soil, plutonium is relatively mobile, transported primarily by colloids. In wet anoxic soils, most of the plutonium is quickly immobilized, although a small fraction remains mobile. The average time plutonium remains in water is proportional to the amount of suspended material. For this reason, more than 90 percent of plutonium is removed from coastal water, while the residence time in mid-ocean water where particulate matter is less is much longer.

Solution Chemistry

The equilibration problems of plutonium are among the most complex encountered in radiochemistry. Of the five oxidation states that plutonium may have, the first four are present in solution as Pu^{+3}, Pu^{+4}, PuO_2^{+1}, PuO_2^{+2}. They coexist in dilute acid solution, and sometimes all four are present in substantial quantities. Problems of disproportionation and auto-oxidation in freshly prepared solutions also complicate the chemistry of plutonium. The (VII) state can form in alkaline solutions, and it has been suggested that the ion in solution is PuO_5^{-3}. Plutonium ions tend to hydrolyze and form complex ions in solution. The +4 ion can form long chain polymers that do not exhibit the usual chemical behavior of the +4 oxidation state. Finally, the different oxidation states exhibit radically different chemical behavior. As a result of these effects, it is possible to mix a plutonium sample with plutonium tracer, subject the mixture to a relatively severe chemical treatment using hot acids or similar reagents, and still selectively recover portions of either the tracer or the sample. This characteristic explains the challenge in achieving reproducible radiochemical results for plutonium.

OXIDATION-REDUCTION BEHAVIOR. Numerous redox agents are available to oxidize and reduce any of the five states of plutonium to alternate oxidation states. Table 14.19 provides a convenient method of preparation of each state and illustrates the use of redox reagents in plutonium chemistry.

Table 14.19 — Redox agents in plutonium chemistry

Oxidation State	Form	Method of Preparation
+3	Pu^{+3}	Dissolve Pu metal in HCl and reduce Pu^{+4} with NH_2OH, N_2H_4, SO_2, or by cathodic reduction
+4	Pu^{+4}	Oxidize Pu^{+3} with hot HNO_3; treat Pu^{+3} or PuO_2^{+2} with NO_2^{-1}
+4	$PuO_2{\cdot}nH_2O$ (polymer)	Heat Pu^{+4} in very dilute acid; peptize $Pu(OH)_4$
V	PuO_2^{+1}	Reduce PuO_2^{+2} with stoichiometric amount of I^{-1} or ascorbic acid; electrolytic reduction of PuO_2^{+2}
VI	PuO_2^{+2}	Oxidize Pu^{+4} with hot dilute HNO_3 or AgO; ozonize Pu^{+4} in cold dilute HNO_3 with Ce^{+3} or Ag^{+1} catalyst
VII	PuO_5^{-3}	Oxidize PuO_2^{+2} in alkali with O_3, $S_2O_8^{-2}$ or radiation

Unlike uranium, the +3 oxidation state is stable enough in solution to be useful in separation chemistry. Disproportionation reactions convert Pu^{+4} to Pu^{+3} and PuO_2^{+2} releasing H^{+1}. The presence of acid in the solution or complexing agents represses the process. Similarly, PuO_2^{+1} disproportionates producing the same products but with the consumption of H^{+1}. For this reason, PuO_2^{+1} is not predominant in acid solutions. These disproportionation reactions can be involved in redox reactions by other reagents. Instead of direct oxidation or reduction, the disproportionation reaction can occur first, followed by direct oxidation or reduction of one of the products.

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

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

- Boil the combined sample and tracer with a concentrated inorganic acid (e.g., HNO_3) to destroy any +4 polymers that might have formed, and
- Cool and dilute the solution; then rapidly (to avoid reforming polymers) treat the solution with excess iodide ion (solution turns brown or black) to momentarily reduce all of the plutonium to the +3 oxidation state.

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

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

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

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

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

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

The PuO_2^{+1} ion has only a slight tendency to hydrolyze, beginning at pH 8, but study of the extent of the process is inhibited by the rapid disproportionation of hydrolyzed plutonium(V).

Hydrolysis of PuO_2^{+2} is far more extensive than expected for a large +2 ion. Hydrolysis begins at pH of about 2.7 to 3.3, giving an orange color to the solution that yields to bright yellow by pH 5. Between pH 5 and 7, dimerizatons seem to occur, and by pH 13 several forms of plutonium hydroxide have been precipitated with solubility products of approximately 2.5×10^{-25}.

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

$$Pu^{+4} > Pu^{+3} \approx PuO_2^{+2} > PuO_2^{+1}$$

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

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

Complexation is preferably through oxygen and fluorine rather than nitrogen, phosphorus, or sulfur. Plutonium also forms complexes with ligands such as phosphate, acetate, and TBP. Strong chelate complexes form with EDTA, tartrate, citrate, TTA, acetylacetone (acac), and cupferron. Pu^{+4} forms a strong complex with fluoride (PuF^{+3}) that is used to solubilize plutonium oxides and keep it in the aqueous phase during extraction of other elements with organic solvents. The complex with nitrate, $Pu(NO_3)_6^{-2}$, allows the recovery of plutonium from nuclear fuels. Carbonate and acetate complexes prevent precipitation of plutonium from solution even at relatively high pH.

Dissolution of Samples

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

Separation Methods

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

PRECIPITATION AND COPRECIPITATION. Macro quantities of plutonium are readily precipitated from aqueous solution, and the methods are the basis of separating plutonium from other radionuclides in some procedures. Contamination of other metals can be a problem, however; zirconium and ruthenium give the most trouble. Plutonium is precipitated primarily as the hydroxide, fluoride, peroxide, or oxalate. Both Pu^{+3} and Pu^{+4} are precipitated from acid solution by potassium or ammonium hydroxide as hydrated hydroxides or hydrous oxides. On redissolving in acid, Pu^{+4} tends to form the polymer, and high concentration of acid is needed to prevent its formation. Pu^{+4} peroxide is formed on the addition of hydrogen peroxide to Pu^{+3}, Pu^{+4}, Pu(V), and Pu(VI) because of the oxidizing nature of hydrogen peroxide. The procedure has been used to prepare highly pure plutonium compounds from americium and uranium.

Coprecipitation of plutonium can be very specific with the control of its oxidation states and selection of coprecipitating reagents. Lanthanum fluoride, a classical procedure for coprecipitation of plutonium, will bring down Pu^{+3} and Pu^{+4} but not Pu(VI). Only elements with similar redox and coprecipitation behavior interfere. Separation from other elements as well as concentration from large volumes with lanthanum fluoride is also important because not many elements form acid-soluble lanthanum fluoride coprecipitates. Bismuth phosphate ($BiPO_4$) is also used to coprecipitate Pu^{+3} and Pu^{+4}. In contrast to lanthanum fluoride and bismuth phosphate, zirconium phosphate [$Zr_3(PO_4)_4$] and an organic coprecipitate, zirconium phenylarsenate [$Zr(C_6H_5)AsO_4$], will coprecipitate Pu^{+4} exclusively.

SOLVENT EXTRACTION. A wide variety of organic extractants have been developed to separate plutonium from other radionuclides and metals by selectively extracting them from aqueous media. The extractants, among others, include organophosphorus compounds such as phosphates (organoesters of phosphoric acid), amines and their quaternary salts, alcohols, ketones, ethers, and amides. Chelating agents such as TTA and cupferron have also been used. Numerous studies have been performed on the behavior of these systems. It has been found that the performance of an extracting system is primarily related to the organic solvent in which the extractant is dissolved and the concentration of the extractant in the solvent, the nature of the aqueous medium (the acid present and its concentration [pH] and the presence of salting agents), the temperature of the system, and the presence and nature of oxidizing agents. One common system, used extensively in the laboratory and in industrial process to extract plutonium from fission products, illustrates the use of solvent extraction to separate plutonium from uranium and other metals. The PUREX process (plutonium uranium reduction extraction) is used in most fuel reprocessing plants to separate the radionuclides. It employs TBP, tri-*n*-butyl phosphate [$(C_4H_9O)_3PO$], in a hydrocarbon solvent, as the extractant. The uranium fuel is dissolved in nitric acid as Pu^{+3}, and plutonium is oxidized to Pu^{+4} and uranium to U(VI) by oxidizing agents. Plutonium and uranium are extracted into a 30 percent TBP solution, and the organic phase is scrubbed with nitric acid solution to remove impurities. The plutonium is removed by back-extracting it as Pu^{+3} with a nitric acid solution containing a reducing agent.

Solvent extraction chromatography, which uses an inert polymeric material as the support for adsorbed organic chelating agents, has provided an efficient, easy technique for rapidly separating plutonium and other transuranic elements. A process using CMPO in TBP and fixed on an inert polymeric resin matrix has been used to isolate Pu^{+4}. Aliquat-336® also has been used successfully. All plutonium in the analyte is adjusted to Pu^{+4}, and the column is loaded from 2 M nitric acid. Plutonium is eluted with 4 M hydrochloric acid and 0.1 M hydroquinone or 0.1 M ammonium hydrogen oxalate ($NH_4HC_2O_4$). Environmental samples contain Fe^{3+} that may interfere with this process and subsequently interfere with the analysis for plutonium. Ascorbic acid can be used to reduce Fe^{+3} to Fe^{+2}, which also reduces Pu^{+4} to Pu^{+3}. Alternatively, nitrite may be added after the ascorbic acid, which will not oxidize the iron but will convert the Pu^{+3} to Pu^{+4}. This process is an example of selective oxidation-reduction of plutonium and iron, and is used in many different separation schemes for plutonium, including separation from americium.

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

Anion-exchange chromatography is one of the primary methods for the separation of plutonium from other metals and the separation of the plutonium oxidation states. On a strong anion-exchange resin, for example, exchange of the higher oxidation states (+4, V, and VI) occurs at hydrochloric acid concentrations above 6 M, while elution occurs at 2 M acid. Plutonium (+3) does not absorb on the column, and Pu(VI) absorbs from 2 to 3 M hydrochloric acid solution. Plutonium can be separated from other actinides and most other elements by exchanging the plutonium cations—Pu^{+4} and Pu(VI)—onto a strong-anion resin from 6 M hydrochloric acid, and subsequently eluting the plutonium by reducing it to Pu^{+3}. Plutonium (+4) may be separated effectively on anion exchange resin in 7-8 M nitric acid as the $[Pu(NO_3)_6]^{-2}$ complex. Uranium will elute slowly in this media, and sufficient volume must be processed in order to avoid cross contamination of uranium with plutonium when the plutonium is subsequently eluted. Elution is achieved at a lower acid concentration, or by reduction to Pu^{+3}.

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

Methods of Analysis

Once isolated, purified, and in solution, ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu are collected for analysis either by electrodepositon on a platinum or nickel disc or by microprecipitation with lanthanum or neodymium fluoride. Mass spectrometry also can be used for longer-lived isotopes of plutonium. Radionuclides of ^{238}Pu, ^{239}Pu, and ^{240}Pu are determined by alpha spectrometry or gas flow proportional counting. Plutonium-241 measured by gas proportional counting. Plutonium-236 and ^{242}Pu are used as tracers for measuring chemical yield.

When analyzing most samples containing ^{238}Pu or ^{239}Pu, the analyst can use either ^{236}Pu or ^{242}Pu as a tracer. However, ^{242}Pu should be avoided as a tracer when analyzing samples that inherently contain ^{242}Pu, such as waste generated by commercial nuclear reactors. When analyzing samples that have higher (> 1 Bq) activity levels of ^{238}Pu or ^{239}Pu, most laboratories will use ^{236}Pu as a tracer because its higher-energy alpha-energy peaks (5.768 and 5.721 MeV) are well separated from the lower energy peaks of ^{238}Pu (highest alpha energy of 5.499 MeV) or ^{239}Pu. Thus, the isolated peaks of the ^{236}Pu tracer can be quantified easily,[1] and any minimum amount of ^{236}Pu peak tailing into the lower energy peaks of ^{238}Pu or ^{239}Pu (containing appreciably more counts) will not significantly affect their quantification. However, when analyzing samples containing very low concentrations of ^{238}Pu or ^{239}Pu (most environmental samples), ^{242}Pu can be used as a

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[1] It should be noted that any contribution from a tracer into the peak(s) of an analyte of interest must be quantified properly, and the affected analyte peak result corrected, to avoid a biased result or Type I error (false positive).

tracer because its highest peak energy of 4.90 MeV is about 0.2 MeV lower than the lowest peak energy of ^{238}Pu or ^{239}Pu. For such low activity samples, the ^{242}Pu activity added to the sample aliquant being processed should be more than the expected ^{238}Pu or ^{239}Pu test source activity. Therefore, any tailing of the ^{239}Pu alpha peaks into the ^{242}Pu peaks would be minimized.

> Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Coleman, 1965; Cotton and Wilkinson, 1988; DOE 1990 and 1997; EPA 1973 and 1980; Maxwell and Fauth, 2000; Metz and Waterbury, 1962; Seaborg and Loveland, 1990; Weigel et al., 1986.

14.10.9.9 Radium

Radium, with an atomic number of 88, is the heaviest (last) member of the family of alkaline earth metals, which, in addition, includes beryllium, magnesium, calcium, strontium, and barium. Radium is the most alkaline and reactive of the series, and exists exclusively as +2 cations in compounds and solution. All isotopes are radioactive, and essentially all analyses are made by radioactive measurements or by mass spectrometry.

Isotopes

There are 25 isotopes of radium, from ^{205}Ra to ^{234}Ra. The most important with respect to the environmental contamination are members of the ^{238}U and ^{232}Th naturally occurring decay series: ^{226}Ra and ^{228}Ra, respectively. Radium-226 ($t_{½} \approx$ 1,602 y) is the most abundant isotopic form. A member of the ^{238}U series, it is produced by alpha emission from ^{230}Th. Radium-226 emits an alpha particle and, in turn, produces ^{222}Rn, an inert gas that is also an alpha emitter. Radium-226 generates radon at the rate of 0.1 µL per day per gram of radium, and its radioactivity decreases at the rate of about 1 percent every 25 years. Radium-228 ($t_{½} \approx$ 5.77 y) is produced in the ^{232}Th decay series by emission of an alpha particle from ^{232}Th itself.

Occurrence

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

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

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

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

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

In groundwater, radium likely encounters dissolved sulfate and/or carbonate anions, which could precipitate radium sulfate or radium carbonate. Although both salts are relatively insoluble, a sulfate concentration of 0.0001 M would still allow an equilibrium concentration of about 0.1

ppm Ra^{+2} to exist in solution. Thus, the insolubilities of either of these salts are not likely to prevent contamination of the environment.

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

Solubility of Compounds

The solubility of radium compounds can usually be inferred from the solubility of the corresponding barium compound and the trend in the solubilities of the corresponding alkaline earth compounds. The common water-soluble radium salts are the chloride, bromide, nitrate, and hydroxide. The fluoride, carbonate, phosphate, biphosphate (hydrogen phosphate), and oxalate are only slightly soluble. Radium sulfate is the least soluble radium compound known, insoluble in water and dilute acids, but it is soluble in concentrated sulfuric acid, forming a complex ion with sulfate anions, $Ra(SO_4)_2^{-2}$.

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

Review of Properties

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

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

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

Solution Chemistry

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

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

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

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

ADSORPTION. The adsorption of trace amounts of radium on surfaces is an important consideration in its radiochemistry. Although not as significant with radium as with some ions with higher charges, serious losses from solution can occur under certain conditions. Adsorption on glass is a particular problem, and adsorption on polyethylene has been reported. Adsorption gradually increases with increasing pH and depends strongly on the nature of the surface. In the extreme, up to 50 percent radium has been observed to adsorb onto glass from neutral solution in 20 days, and 30 percent from 0.13 M hydrochloric acid (HCl). Fortunately, adsorbed radium can be removed from glass with strong acid.

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

Dissolution of Samples

Soil, mineral, ore samples, and other inorganic solids are dissolved by conventional treatment with mineral acids and by fusion with sodium carbonate (Na_2CO_3). Hydrofluoric acid (HF) or potassium fluoride (KF) is used to remove silica. Up to 95 percent radium removal has been leached from some samples with hot nitric acid (HNO_3), but such simple treatment will not completely dissolve all the radium in soil, rock, and mineral samples. Biological samples are wet ashed first with mineral acids or decomposed by heating to remove organic material. The residue is taken up in mineral acids or treated to remove silica. Any dissolution method that results in two or more separate fractions should be avoided, because the adsorption characteristics of trace quantities of radium may cause it to divide between the fractions.

Barium sulfate ($BaSO_4$), often used to coprecipitate radium from solution, can be dissolved directly into alkaline EDTA solutions. Radium can be repeatedly reprecipitated and dissolved by alternate acidification with acetic acid and dissolution with the EDTA solution.

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

Separation Methods

COPRECIPITATION. Radium is almost always present in solution in trace amounts, and even the most insoluble radium compound, radium sulfate, can not be used to separate and isolate radium from solution by direct precipitation. Therefore, the cation is commonly removed from solution in virtually quantitative amounts by coprecipitation. Because radium forms the same types of insoluble compounds as barium: sulfates (SO_4^{-2}), chromates (CrO_4^{-2}), carbonates (CO_3^{-2}), phosphates (PO_4^{-3}), oxalates ($C_2O_4^{-2}$), and sulfites (SO_3^{-2}), it coprecipitates with all insoluble barium compounds, and to a lesser extent with most insoluble strontium and lead compounds. Barium sulfate and barium chromate are most frequently used to carry radium during coprecipitation. Other compounds that are good carriers for radium include: ferric hydroxide when precipitated at moderately high pH with sodium hydroxide (NaOH) or ammonium hydroxide (NH_4OH), barium chloride ($BaCl_2$) when precipitated from a cold mixed solvent of water and alcohol saturated with hydrochloric acid, barium iodate [$Ba(IO_3)_2$], and various insoluble phosphates, fluorides, and oxalates (e.g., thorium phosphate [$Th_3(PO_4)_4$], lanthanum fluoride (LaF_3), and thorium oxalate [$Th(C_2O_4)_2$]. Lead sulfate ($PbSO_4$) can be used if a carrier-free radium preparation is required, because quantitative lead-radium separations are possible while quantitative barium-radium separations are very difficult.

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

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

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

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

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

Methods of Analysis

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

Radium-228 can also be determined directly by gamma spectroscopy, using the gamma-rays of its progeny, ^{228}Ac, without concern for interference. Alower detection limit is obtained if the ^{228}Ac is measured by beta counting. In the beta-counting procedure, ^{228}Ra is separated, time is allowed for actinium ingrowth, the ^{228}Ac is removed by solvent extraction, ion-exchange, or coprecipitation, and then measured by beta counting.

Radium-224 can be determined by chemically isolating the ^{212}Pb, which is in equilibrium with the ^{224}Ra. After an appropriate ingrowth period, ^{212}Pb is determined by alpha-, beta-, or gamma-counting its progeny, ^{212}Bi and ^{212}Po.

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

14.10.9.10 Strontium

Strontium, atomic number 38, is the fourth member of the alkaline-earth metals, which includes beryllium, magnesium, calcium, strontium, barium, and radium. Like radium, it exists exclusively in the +2 oxidation state in both compounds and in solution, making its chemistry simpler than many of the radionuclides reviewed in this section.

Isotopes

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

Occurrence and Uses

Strontium is found in nature in two main ores, celestite ($SrSO_4$) and strontianite ($SrCO_3$), widely distributed in small concentrations. Small amounts are found associated with calcium and barium minerals. The Earth's crust contains 0.042 percent strontium, ranking twenty-first among the elements occurring in rock and making it as abundant as chlorine and sulfur. The element ranks eleventh in abundance in sea water, about 8–10 ppm. The only naturally occurring radioactive isotopes of strontium are the result of spontaneous fission of uranium in rocks. Other nuclear reactions and fallout from nuclear weapons test are additional sources of fission products. Strontium-90 is a fission product of ^{235}U, along with ^{89}Sr, and short-lived isotopes, ^{91}Sr to ^{102}Sr. Strontium-85 can be produced by irradiation of ^{85}Rb with accelerated protons or deuterons.

The beta emission of ^{90}Sr and its progeny, ^{90}Y ($t_{½} \approx 64$ h), has found applications in industry, medicine, and research. The radionuclides are in equilibrium in about 25 days. The radiation of ^{90}Y is more penetrating than that of strontium. It is used with zinc sulfide in some luminescent paints. Implants of ^{90}Sr provide radiation therapy for the treatment of the pituitary gland and breast and nerve tissue. The radiation from strontium has been used in thickness gauges, level measurements, automatic control processes, diffusion studies of seawater, and a source of electrical power. Because ^{90}Sr is one of the long-lived and most energetic beta emitters, it might prove to be a good source of power in space vehicles, remote weather stations, navigational buoys, and similar long-life, remote devices. Both ^{89}Sr and ^{90}Sr have been used in physical chemistry experiments and in biology as tags and tracers. Ratios of ^{88}Sr to ^{87}Sr ratios are used in geological dating, because ^{87}Sr is formed by decay of long-lived ^{87}Rb.

Solubility of Compounds

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

Review of Properties

Strontium is a low-density (2.54 g/cm^3) silver-white metal. It is as soft as lead and is malleable and ductile. Three allotropic forms exit with transition temperatures of 235 and 540 °C. Freshly cut strontium is silver in appearance, but it rapidly turns a yellowish color on formation of the oxide in air. It is stored under mineral oil to prevent oxidation.

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

Strontium occurring in groundwater is primarily in the form of divalent strontium ions. Its solubility under oxidizing and reducing conditions is approximately 0.001 M (0.15 g/L or 150 g/m^3).

Solution Chemistry

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

COMPLEXATION. Strontium has little tendency to form complexes. Of the few complexing agents for strontium, the significant agents in radiochemistry to date are EDTA, oxalate, citrate, ammoniatriacetate, methylanine-N,N-diacetate, 8-quinolinol, and an insoluble chelate with picrolonate. The most stable complex ion forms with EDTA. Coordination compounds of strontium are not common. These chelating agents are used primarily in ion-exchange procedures. Amine chelates of strontium are unstable, and the β-diketones and alcohol chelates are poorly characterized. In contrast, cyclic crown ethers and cryptates form stronger chelates with strontium than with calcium, the stronger chelating metal with EDTA and more traditional chelating agents. Cryptates are a macrocyclic chelate of the type, $N[(CH_2CH_2O)_2CH_2CH_2]_3N$, an octadentate ligand containing six oxygen atoms and two nitrogen atoms as ligand bonding sites that encapsulates the cation. It might find use in the extraction chemistry of strontium.

HYDROLYSIS. The tendency of the alkaline-earth cations to hydrolyze decreases as their atomic number increases. The tendency is greater than that of the corresponding alkali metals, but hydrolysis of potassium, for example, is insignificant. An indication of the tendency of a cation to hydrolyze is the solubility of their hydroxides, and the solubility of the alkaline earths increases with increasing atomic number. Strontium hydroxide is slightly soluble in water (8 g/L at 20 °C). In comparison, the hydroxide of beryllium, the first element in the alkaline earth series, has a solubility of approximately 3×10^{-4} g/L.

Dissolution of Samples

Dissolution of samples for the analysis of strontium is generally simple. Water is used to dissolve soluble compounds: acetate, bromide, chloride, iodide, chlorate, perchlorate, nitrate, nitrite, and permangenate. Hydrochloric or nitric acid dissolves the fluoride, carbonate, oxalate, chromate, phosphate, sulfate, and oxide. Strontium in limestone, cement, soil, bone, and other biological material can be dissolved from some samples in hot hydrochloric acid. Insoluble silica, if present, can be filtered or centrifuged. In some cases, soil can be leached to remove strontium. As much as 99.5 percent of the strontium in some crushed soil samples has been leached with 1 M nitric acid by three extractions. Soil samples have also been suspended overnight in ammonium acetate at pH 7 to leach strontium. If leaching is not successful, soil samples can be dissolved by alkali fusion of the ground powder with potassium hydroxide, nitrate, or carbonate. Strontium is taken up from the residue in nitric acid. Biological materials such as plant material or dairy products are solubilized by ashing at 600 °C and taking up milk residue in hot, concentrated hydrochloric acid and plant residue in aqua regia. Wet ashing can be used by treating the sample with nitric acid followed by an equal-volume mixture of nitric and perchloric acids. Human and animal bone samples are ashed at 900 °C and the residue dissolved in concentrated hydrochloric acid.

Separation Methods

PRECIPITATION AND COPRECIPITATION. The common insoluble salts of strontium are the fluoride, carbonate, oxalate, chromate, and sulfate. Most are suitable for radiochemical procedures, and strontium separation have the advantage of stable forms of strontium that can be used as a carrier and are readily available. Precipitation of strontium nitrate in 80 percent nitric acid has been used to separate stable strontium carrier and ^{90}Sr from its progeny, ^{90}Y, and other soluble nitrates (calcium, for example). The solubility of strontium chloride in concentrated hydrochloric solution has been used to separate strontium from barium—barium chloride is insoluble in the acid. Barium and radium (as coprecipitant) have been removed from strontium by precipitating barium as the chromate at a carefully controlled pH of 5.5. Strontium chromate will not precipitate unless the pH is raised. Strontium can also be separated from yttrium by precipitation of the much less soluble yttrium hydroxide by raising an acid solution of the cations to a pH of about 8 with ammonium hydroxide. Strontium hydroxide is slightly soluble and will not precipitate without high concentrations of hydroxide or strontium or both. Carrier-free strontium is coprecipitated with ferric hydroxide, and lead sulfate is also used.

SOLVENT EXTRACTION. The application of organic solvents for separation of strontium from other metals has not been extensive. TTA has been used to extract carrier-free strontium at a pH greater than 10. At pH 5, ^{90}Y is extracted with TTA from strontium, which remains in aqueous solution. 8-hydroxyquinolinol in chloroform has also been used to extract strontium. The few procedures that have been available are mainly used to separate the alkaline earths from each other. A 1:1 mixture of ethyl alcohol and diethyl ether with di-2-ethylhexyl phosphoric acid extracts calcium from strontium.

In recent years, extraction procedures have been developed based on the complexation of strontium cations with crown ethers in 1-octanol. Strontium can be extracted with these mixture from 1 M to 7 M nitric acid solutions. The most advantageous application of strontium extraction procedures has been found in extraction chromatography. An extraction resin consisting of 4,4'(5')-bis(*t*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) in 1-octanol on an inert polymeric matrix is highly selective for strontium nitrate and will separate the cation from many other metals including calcium, barium, and yttrium. This column is used to separate strontium from potassium, cerium, plutonium, and neptunium (K^{+1}, Ce^{+4}, Pu^{+4}, Np^{+4}, respectively). The column is prepared and loaded from 8 M nitric acid. The ions listed above are eluted with 3 M nitric acid containing oxalic acid. Strontium is eluted with 0.05 M nitric acid.

ION-EXCHANGE CHROMATOGRAPHY. Ion-exchange chromatography is used to separate trace quantities of strontium, but separation of macro quantities is very time consuming. Strontium is absorbed on cation-exchange resins, and elution is often based on the formation of a stable complex. Carrier-free strontium is separated from fission products, including barium, on a cation-exchange resin and eluted with citrate. In a similar process, strontium was also separated from other alkaline earths, magnesium, calcium, barium, and radium, eluting with ammonium lactate at pH 7 and 78 °C. Good separations were also obtained with hydrochloric solutions and ammonium citrate. Strontium-90 and ^{90}Y are separated on a cation-exchange column, eluting yttrium with ammonium citrate at pH 3.8 and strontium at pH 6.0. Strontium and calcium have also been separated in EDTA solutions at pH 5.3. Strontium is retained on the column, and calcium elutes as the calcium-EDTA complex. Strontium elutes with 3 M hydrochloric acid.

Strontium does not form many anionic complextes, Thus, not many procedures use anion-exchange chromatography for separation of strontium. Strontium-90 has been separated from ^{90}Y on an anion-exchange resin pretreated with hydroxide. Strontium is eluted from the column with water, and yttrium is eluted with 1 M hydrochloric acid. The alkaline earths have been separated by anion-exchange column pretreated with dilute ammonium citrate, loading the column with the chloride form of the metals, and eluting with ammonium citrate at pH 7.5.

Methods of Analysis

Macroquantities of strontium are determined by gravimetric methods and atomic absorption spectrometry, and emission spectrometry. Strontium is precipitated as strontium carbonate or sulfate in gravimetric procedures. For atomic absorption analysis, the separated sample is ashed, and the product is dissolved in hydrochloric acid. Lanthanum is added to the solution to precipitate interfering anions, phosphate, sulfate, or aluminate, that would occur in the flame.

Strontium-89 and ^{90}Sr are determined by analysis of their beta emissions. With a short half-life of 50.5 d, ^{89}Sr is only found in fresh fission products. Strontium-90 is a beta emitter with a half-life of 27.7 y. Its progeny is ^{90}Y, which emits beta particles with a half-life of 64.0 h, producing stable ^{90}Zr. Neither ^{90}Sr nor ^{90}Y is a gamma emitter. Strontium-90 is determined directly from its beta emission, before ^{90}Y grows in, by beta counting immediately (three to four hours) after it is collected by precipitation. The chemical yield can be determined gravimetrically by the addition of stable strontium, after the separation of calcium. Alternatively, ^{90}Sr can be measured from the beta emission of ^{90}Y while it reaches secular equilibrium (two to three weeks). The ^{90}Y is separated by solvent extraction and evaporated to dryness or by precipitation, then beta counted. The chemical yield of the yttrium procedure can be determined by adding stable yttrium and determining the yttrium gravimetrically. Strontium-89 has a half-life of 50.5 d and is only present in fresh fission material. If it is present with ^{90}Sr, it can be determined by the difference in activity of combined ^{89}Sr and ^{90}Sr (combined or total strontium) and the activity of ^{90}Sr. Total strontium is measured by beta counting immediately after it is collected by precipitation, and ^{90}Sr is measured by isolating ^{90}Y after ingrowth. Strontium-85 can be used as a tracer for determining the chemical yield of ^{90}Sr (determined by isolating ^{90}Y), but its beta emission interferes with beta counting of total strontium and must be accounted for in the final activity.

An alternative method for determining ^{89}Sr and ^{90}Sr in the presence of each other is based on the equations for decay of strontium radionuclides and ingrowth of ^{90}Y. Combined strontium is collected and immediately counted to determine the total strontium. During ingrowth, the mixture is recounted, and the data from the counts are used to determine the amount of ^{89}Sr and ^{90}Sr in the original (fresh) mixture.

Cerenkov radiation counting techniques also may be used for $^{89/90}$Sr analysis. When beta particle energies exceed the speed of light in the medium in which the beta particles are emitted, the excess energy is emitted in the energy range of 350-600 nm. In water, the energy to be exceeded is 0.263 MeV. As a practical matter, however, Cerenkov radiation counting is not very useful for beta energies less than 1 MeV beta maximum ($E_{\beta\mathrm{max}}$) typically found in environmental laboratories. NCRP (1985) cites a 3 percent detection efficiency for a ^{204}Tl $E_{\beta\mathrm{max}}$ of 0.764 MeV, with corresponding average beta energy of 0.240 MeV. Only at a ^{143}Pr of 0.932 MeV does the detection efficiency go to 6.2 percent—a detection efficiency of marginal usefulness as a figure of merit.

The three isotopes that are involved with this analysis are ^{89}Sr ($E_{\beta max}$ = 1.5 MeV), ^{90}Sr ($E_{\beta max}$ = 0.5 MeV), and ^{90}Y ($E_{\beta max}$ = 2.3 MeV). The analysis requires chemical separation of the strontium from the sample matrix by conventional techniques. Cerenkov counting relies on the beta energies (the ^{90}Sr beta does not contribute significantly). For example, strontium may be separated chemically as an oxalate precipitate (after yttrium has been removed by precipitation), dissolved in nitric acid, and counted immediately (yielding the counts for ^{89}Sr). After about 10 days, the sample would be recounted, yielding a total for ^{89}Sr + ^{90}Y. The value for the ^{90}Y is then determined by applying spectral interference factors for spectral overlap and appropriate background subtraction techniques. Alternatively, ^{90}Y can be separated from the strontium solution after a period of ingrowth and Cerenkov-counted to determine the ^{90}Sr concentration.

> Compiled from: Baes and Mesmer, 1976; Banavali et al., 1995; Choppin et al., 1995; Considine and Considine, 1983; CRC, 1998-99; DOE, 1990 and 1997, 1997; EPA, 1973; EPA, 1980; Greenwood and Earnshaw, 1984; Hassinsky and Adloff, 1965; NCRP, 1985; Riley, 1995; Rucker, 1991; Sunderman and Townley, 1960; Turekian and Bolter, 1966.

14.10.9.11 Sulfur and Phosphorus

The radiochemistry of sulfur and phosphorus is somewhat different than most other radioisotopes. These two elements are nonmetallic and, like carbon, can be found in many different types of compounds. These two elements are used most extensively as tracers by incorporation into organic molecules, generally as covalent-bonded atoms. Thus, they do not react as sulfur or phosphorus, but as the molecule of which they are a part. They may be present as inorganic species, which have their own peculiar chemistry.

Isotopes

Sulfur has 17 isotopes, four of which are stable. Only two of the 13 radioisotopes have significant radiochemical analytical applications. These are ^{35}S ($t_{½}$ ≈87.2 d) and ^{37}S ($t_{½}$ ≈ 5 min). Sulfur-35 decays only by beta emission with no gamma emission. Sulfur-37 decays by beta emission with a 3.1 MeV delayed gamma emission.

Phosphorus also has 17 isotopes, only one of which is stable. Its two principal radioisotopes, ^{32}P ($t_{½}$ ≈ 14.3 d) and ^{33}P ($t_{½}$ ≈ 25.3 d), both decay only by beta emission, with no gamma emission.

Occurrence

None of the radioisotopes of sulfur occurs naturally. They are produced by neutron activation of stable parent isotopes or by accelerator bombardment techniques. Both ^{32}P and ^{33}P are formed naturally in the upper atmosphere. The steady-state concentration of these radionuclides in rainwater is about 0.05 Bq/L. They are also produced artificially by accelerator bombardment.

Solubility and Solution Chemistry

The most stable forms of the two elements in aqueous solutions are sulfate and phosphate. However, the relatively long half-lives of the radioisotopes of S and P allow them to be incorporated easily into organic or biomolecules. In these instances, the chemical identity of the radioisotope is sacrificed for the chemical property of the molecule. For example, ^{35}S may be incorporated into these species, but each will have a distinct chemical property:

$$SO_4^{-2}\text{ , }S^{-2}\text{ , }CH_3\text{-S-}CH_2\text{-}CH_2\text{-C(H)(}NH_2\text{)(COOH)}\ \ \text{[methionine]}$$

$$\text{H-S-}CH_2\text{-C(H)(}NH_2\text{)(COOH) [cystine]}$$

If a solution of methionine had added to it methionine labeled with ^{35}S, the radioisotope-containing molecules would be indistinguishable chemically from the other methionine molecules. However, if the methionine solution was equilibrated with a solution of $^{35}S^{-2}$, no ^{35}S would be found in the methionine molecules, because methionine does not dissociate to give S^{-2}.

Similarly, for phosphorus the radioisotope could be incorporated into the following species:

$$PO_4^{3-},\ \ (C_8H_{17})_3PO\ \text{[tri-}n\text{-octylphosphine oxide]}$$

$$H_2PO_4\text{-}\{C_9H_{14}N_5O_3\}\ \text{[adenosine-5-phosphoric acid].}$$

Here, the tri-*n*-octylphosphine oxide is soluble in organic solvents but not in water, while the other two are readily water-soluble. For the two water-soluble molecules, under conditions of neutral pH, no exchange of radiophosphorus would be expected between them. However under certain conditions where the organic molecule could be hydrolyzed, exchange could occur. Incorporation of the radioisotope into an organic molecule would occur by first forming the radioisotope by nuclear bombardment, then reacting the activated material with the appropriate reagents to form the molecule of interest. Attempting to form the radioisotope by activation of the organic molecule would lead to the destruction of the organic molecule, and the radioisotope would be part of other (potentially) unknown species. The chemical purity of the final product would be verified through an independent means such as infrared, nuclear magnetic resonance, or mass spectrometry. The specific activity of the new molecule then can be calculated by measuring the activity due to the radioisotope.

OXIDATION-REDUCTION. For each of these elements, the most stable ionic form in aqueous solution is as the SO_4^{-2} or the PO_4^{3-} ions (dependent upon pH). Sample oxidation for sulfur should be performed with care to avoid loss as SO_2 or as H_2S. This can occur in nitric acid when sulfides or organic sulfur compounds are present. Oxidation in basic solution using hydrogen peroxide or permanganate can avoid such losses. Phosphorus does not suffer from this disadvantage of acid oxidation. Generally, when present as phosphate or sulfate, reduction to other species will not occur unless powerful reducing agents have been added to the solution.

COMPLEXATION. Neither sulfate nor phosphate are strong complexing agents. This is due to their negative charge being spread out among many atoms, yielding low charge density. Most complexing ions are strongly nucleophilic.

Dissolution of Samples

The radioisotopes of phosphorus and sulfur generally are incorporated into *in vivo* or *in vitro* studies of plant or animal tissues. The cost common methods of sample preparation for these studies usually are maceration/suspension, tissue solubilization, and total oxidation. The method of maceration is a reduction of the "size" of the sample. The material is suspended in a minimal amount of fluid, and then a physical means such as a blender, mortar and pestle, or stirring rod is used to suspend the material in the solvent. The chemical nature of the molecule containing the radioisotope is unchanged.

Tissue solubilization is the addition of a chemical solvent such as toluene, which dissolves the tissue in its entirety putting the sample into an organic solvent matrix. The chemical nature of the molecule containing the radioisotope is unchanged.

Total oxidation is performed most frequently using either peroxide or nitric acid, which removes all of the organic material as carbon dioxide, and the elements are in solution as phosphate or sulfate. Care should be taken in this form of sample preparation for sulfur, because it can be volatilized as SO_2 or SO_3 vapor.

The molecules of interest having biochemical activity may change chemically during the course of such studies. Thus, one should consider what the potential decomposition products are, and how they should be separated from the organic/biomolecules of interest, before preparing the sample. If an environmental sample were to be analyzed for these radioisotopes, the sample preparation would need to be total-sample-oxidation, because the type of organic material would likely be unknown.

Separation Methods

Because many different organic forms exist for these elements, it would be difficult to identify all of the different separation techniques used to separate them from specific mixtures of other organic compounds. Generally, the techniques that are used are HPLC, GC, and electrophoresis. In many instances, separation of the molecules containing the radioisotopes is not necessary, because the sulfur or phosphorus is the only radioisotope present, having been used as a tracer in following the reaction progress or products.

PRECIPITATION. Sulfur may be analyzed by sample oxidation followed by barium precipitation. This takes place at about pH 2 in HCl solution. As with other separation techniques, sample processing should ensure the elimination of other cations (such as radium or strontium), which could be present in environmental samples.

Phosphate is a strong Bronsted-Lowry base. Precipitation of phosphate salts would be carried out best in basic media. However, most metal salts also form insoluble hydroxides, so this form of separation is not used frequently. However, if other metal ions are removed, phosphate can be completely precipitated using calcium ion in basic solution.

ION EXCHANGE. Both phosphate and sulfate may be exchanged easily on anion exchange media. However, if the anion resin were in the hydroxide form, the exchange would release hydroxide and potentially cause precipitation of metal ions either on the ion exchange resin or in the eluent. Thus, converting the anion resin to the nitrate or chloride form prior to separation would permit the free flow of eluent without precipitation. Such separation will occur on weak base anion exchangers (such as those used in ion chromatography) or strong base ion exchangers.

Methods of Analysis

All of the radioisotopes of interest of phosphorus and sulfur are beta emitters. The most effective method of analysis for these isotopes is liquid scintillation. For the analysis of organic/biomolecules, the scintillation cocktail usually may be added directly to the analyte after one of the methods of nonoxidative sample preparation described above. In some instances, these analytes may contain double-labeled compounds. Other radioisotopes, such as ^{14}C or ^{3}H, also may be incorporated into the molecule. These can also be analyzed directly by liquid scintillation because of the significant differences in the beta particle energies. Samples of unknown origin would require oxidation and separation prior to analysis.

14.10.9.12 Technetium

Technetium, atomic number 43, has no stable isotopes. Natural technetium is known to exist but only in negligibly small quantities resulting from the spontaneous fission of natural uranium. Technetium is chemically very similar to rhenium, but significant differences exist that cause them to behave quite differently under certain conditions.

Isotopes

Thirty-one radioisotopes of technetium are known with mass numbers ranging from 86 to 113. The half-lives range from seconds to millions of years. The lower mass number isotopes decay by primarily by electron capture and the higher mass number isotopes by beta emission. The significant isotopes (with half-lives/decay modes) are ^{95m}Tc (61 d/electron capture and isomeric transition), ^{99m}Tc (6.01 h/isomeric transition by low-energy γ), and ^{99}Tc (2.13×10^{5} y/β to stable ^{99}Ru). Other long-lived isotopes are ^{97}Tc (2.6×10^{6}/electron-capture) and ^{98}Tc (4.2×10^{6} y/β emission).

Occurrence and Uses

The first synthesis of technetium was through the production of ^{99}Mo by bombardment of ^{98}Mo with neutrons and subsequent beta decay to ^{99}Tc. Technetium is also a major constituent of nuclear reactor fission products and has been found in very small quantities in pitchblende from the spontaneous fission of naturally occurring uranium.

Technetium makes up about 6 percent of uranium fission products in nuclear power plant fuels. It is recovered from these fuels by solvent extraction and ion-exchange after storage of the fuels for several years to allow the highly radioactive, short-lived products to decay. Technetium is recovered as ammonium pertechnetate (NH_4TcO_4) after its solutions are acidified with hydrochloric acid, precipitated with sulfide, and the sulfide (Tc_2S_7) is reacted with hydrogen peroxide. Rhenium and molybdenum are also removed by extraction with organic solvents. The metal is obtained by reduction of ammonium pertechnetate with hydrogen at 600 °C.

Potassium pertechnetates ($KTcO_4$) have been used in water (55 ppm) as corrosion inhibitors for mild carbon steel in aerated distilled water, but currently there is no significant uses of elemental technetium or its compounds, although technetium and some of its alloys are superconductors. The corrosion protection is limited to closed systems to prevent release of the radioactive isotope. Technetium-95m, with a half-life of only 61 days, has been used in tracer work. Technetium-99m is used in medical diagnosis as a radioactive tracer. As a complex, the amount of ^{99m}Tc required for gamma scanning is very small, so it is referred to as noninvasive scanning. It is used for cardiovascular and brain studies and the diagnosis of liver, spleen, and thyroid disorders. There are more than 20 ^{99m}Tc compounds available commercially for diagnostic purposes. With iodine isotopes, they are the most frequently used radionuclides for diagnostics. Technetium-99m also has been used to determine the deadtime of counting detectors.

Solubility of Compounds

The nature of the compounds has not been thoroughly delineated, but ammonium pertechnetate is soluble in water, and technetium heptoxide forms soluble pertechnetic acid ($HTcO_4$) when water is added.

Review of Properties

Technetium is a silver-grey metal that resembles platinum in appearance. It tarnishes slowly in moist air to give the oxyacid, pertechnetic acid ($HTcO_4$). It has a density of 11.5 g/cm^3. The metal reacts with oxygen at elevated temperatures to produce the volatile oxide, technetium heptoxide. Technetium dissolves in warm bromine water, nitric acid, aqua regia, and concentrated sulfuric acid, but it is insoluble in hydrochloric and hydrofluoric acids. Technetium forms the chlorides ($TcCl_4$ and $TcCl_6$) and fluorides (TcF_5 and TcF_6) by direct combination of the metal with the respective halogen. The specific halide is obtained by selecting the proper temperature and pressure for its formation.

The behavior of technetium in groundwater is highly dependent on its oxidation state. Under oxidizing conditions, pertechnetate is the predominant species. It is very soluble and only slightly absorbed to mineral components. For those reasons, it has a relatively high dissemination potential in natural systems. Under reducing conditions, technetium precipitates as technetium dioxide (TcO_2), which is very insoluble. With the production of ^{99}Tc in fission fuels and considering its long half-life, the soluble form of the radionuclide is an environmental concern wherever the fuel is reprocessed or stored. As a consequence, ^{99}Tc would be expected to be one of the principal contributors to a radioactive release to the environment, even from repositories with barriers that could retain the radionuclide up to 10,000 years. Studies of a salt repository indicate that ^{99}Tc is one of the few radionuclides that might reach the surface before it decays.

Solution Chemistry

All oxidation states between −1 and +7 can be expected for technetium, but the important ones in solution are +4 and +7. The +4 state exist primarily as the slightly soluble oxide, TcO_2. It is soluble only in the presence of complexing ligands; $TcCl_6^{-2}$, for example, is stable in solutions with a chloride concentration greater than 1 M. The most important species in solution is the pertechnetate ion [TcO_4^{-1} as Tc(VII)], which is readily soluble and easily formed from lower oxidation states with oxidizing agents such as nitric acid and hydrogen peroxide. There is no evidence of polymeric forms in solution as a result of hydrolysis of the metal ion.

OXIDATION-REDUCTION BEHAVIOR. Most radioanalytical procedures for technetium are performed on the pertechnetate ion, TcO_4^{-1}. The ion can be reduced by hydrochloric acid, the thiocyanate ion (SCN^{-1}), organic impurities, anion-exchange resins, and some organic solvents. The product of reduction can be TcO_2 [Tc^{+4}], although a multiplicity of other products are expected in complexing media. Even though the +7 oxidation state is easy to reduce, the reduction process is sometimes slow. Unless precautions are taken to maintain the appropriate oxidation state, however, erratic results will be obtained during the radioanalytical procedure. Several examples illustrate the precaution. Dissolution should always be performed under strongly oxidizing conditions to ensure conversion of all states to the +7 oxidation state because complications because of slow exchange with carrier and other reagents are less likely to occur if this state is maintained. Technetium is extracted with various solvents in several radioanalytical procedures, but the method can be very inefficient because of reduction of the pertechnetate ion by some organic solvents. The presence of an oxidizing agent such as hydrogen peroxide will prevent the unwanted reduction. In contrast, TcO_4^{-1} is easily lost on evaporation of acid solutions unless a reducing agent is present or evaporation is conducted at a relatively low temperature.

COMPLEXATION. Technetium forms complex ions in solution with several simple inorganic ligands such as fluoride and chloride. The +4 oxidation state is represented by the TcX_6^{-2} ion where X = F, Cl, Br, and I. It is formed from TcO_4^{-1} by reduction to the +4 state with iodide in

HX. TcF_6^{-2} is found in HF solutions during decomposition of samples, before further oxidation.

Complex ions formed between organic ligands and technetium in the (V) oxidation state are known with the general formula, TcO_3XLL, where X is a halide and L is an organic ligand. the ligands typically bond through an oxygen or nitrogen atom. Other organic complexes of the (V) state have the general formulas: $TcOX_2L_2$, $TcOX_4^{-1}$, and $TcOX_5^{-2}$.

Dissolution of Samples

Dissolution of samples containing technetium requires two precautions: it is essential that acid solutions be heated only under reflux conditions to avoid losses by volatilization, and dissolution should be done only with strongly oxidizing conditions to ensure conversion of all lower oxidation states to Tc(VII). In addition, problems with slow carrier exchange are less likely for the (VII) oxidation state. Molybdenum targets are dissolved in nitric acid or aqua regia, but the excess acid interferes with many subsequent analytical steps. Dissolution in concentrated sulfuric acid followed by oxidation with hydrogen peroxide after neutralization avoids these problems of excess acid. Other technetium samples can be dissolved by fusion with sodium peroxide/sodium hydroxide (Na_2O_2/NaOH) fluxes.

Separation Methods

PRECIPITATION AND COPRECIPITATION. The various oxidation states of technetium are precipitated in different forms with different reagents. Technetium(VII) is primarily present in solution as the pertechnetate anion, and macro quantities are precipitated with large cations such as thallium (Tl^{+1}), silver (Ag^{+1}), cesium (Cs^{+1}), and tetraphenylarsonium [$(C_6H_5)_4As^{+1}$]. the latter ion is the most efficient if ice-bath conditions are used. Pertechnetate is coprecipitated without interference from molybdenum with these cations and perrhenate (ReO_4^{-1}), perchlorate (ClO_4^{-1}), periodate (IO_4^{-1}), and tetrafluoroborate (BF_4^{-1}). The salt consisting of tetraphenylarsenium and the perrhenate froms a coprecipitate fastest, in several seconds. Technetium(VII) can be precipitated from solution as the heptasulfide (Tc_2S_7) by the addition of hydrogen sulfide (or hydrogen sulfide generating compounds such as thioacetamide and sodium thiosulfate) from 4 M sulfuric acid. Because many other transition metals often associated with technetium also from insoluble compounds with sulfide, the method is primarily used to concentrate technetium.

Technetium (+4) is carried by ferric hydroxide. The method can be use to separate technetium from rhenium. The precipitate is solubilized and oxidized with concentrated nitric acid, and iron is removed by precipitation with aqueous ammonia. Technetium is coprecipitated as the hexachlorotechnetate (+4) ($TcCl_6^{-2}$) with thallium, and rhenium as the α,α'-dipyridylhexachlororhenate (+4).

Technetium(VI) (probably as TcO_4^{-2}) is carried quantitatively by molybdenum 8-hydroxyquinolate and by silver or lead molybdate. Tc^{+3} is carried quantitatively by iron or zinc hydroxide and the sulfide, hydroxide, and 8-hydroxyquinolate of molybdenum.

SOLVENT EXTRACTION. Technetium, primarily in the Tc(VII) state (pertechnetate) can be isolated by extraction with organic solvents, but the principal disadvantage of all extraction systems is the inevitable introduction of organic material that might reduce the pertechnetate anion and cause difficulties in subsequent analytical steps. The pertechnetate ion is extracted with pyridine from a 4 M sodium hydroxide solution, but perrhenate and permanganate ions are also extracted. The anion also extracts into chloroform in the presence of the tetraphenylarsonium ion as tetraphenylarsonium pertechnetate. Extraction is more favorable from neutral or basic sulfate solutions than chloride solutions. Perrhenate and perchlorate are also extracted but molybdenum does not interfere. Small amounts of hydrogen peroxide in the extraction mixture prevent reduction of pertechnetate. Technetium is back-extracted into 0.2 M perchloric acid or 12 M sulfuric acid. Other organic solvents are have also been used to extract pertechnetate from acid solutions, including alcohols, ketones, and tributyl phosphate. Ketones and cyclic amines are more effective for extraction from basic solutions. Tertiary amines and quaternary ammonium salts are more effective extracting agents than alcohols, ketones, and tributyl phosphate. Back extraction is accomplished several ways, depending on the extraction system. A change in pH, displacement by another anion such as perchlorate, nitrate, or bisulfate, or addition of a nonpolar solvent to an extraction system consisting of an oxygen-containing solvent.

A recent extraction method has been used successfully for extraction chromatography and extractive filtration. A column material consisting of trioctyl and tridecyl methyl ammonium chlorides impregnated in an inert apolar polymeric matrix is used to separate ^{99}Tc by loading the radionuclide as the pertechnetate ion from a 0.1 M nitric acid solution. It is stripped off the column most readily with 12 M nitric acid. Alternatively, the extraction material is used in a filter disc, and the samples containing ^{99}Tc are filtered from water at pH 2 and rinsed with 0.01 M nitric acid. Technetium is collected on the disc.

Lower oxidation states of technetium are possible. The thiocyanate complexes of technetium(V) are soluble in alcohols, ethers, ketones, and trioctylphosphine oxide or trioctylamine hydrochloride in cyclohexane or 1,2-dichloroethane. Technetium (+4), as $TcCl_6^{-2}$, extracts into chloroform in the presence of high concentrations of tetraphenylarsonium ion. Pertechnetate and perrhenate are both extracted from alkaline solution by hexone (methyl isobutyl ketone), but reduction of technetium to the +4 state with hydrazine or hydroxylamine results in the extraction of perrhenate only.

ION-EXCHANGE CHROMATOGRAPHY. Ion-exchange chromatography is primarily performed with technetium as the pertechnetate anion. Technetium does not exchange on cation resins, so technetium is rapidly separated from other cations on these columns. In contrast, it is strongly absorbed on strong anion exchangers and is eluted with anions that have a greater affinity for the resin. Technetium and molybdenum are separated using ammonium thiocyanate as the eluent. A good separation of pertechnetate and molybdate has been achieved on an anion-exchange resin in the phosphate form where the molybdate is preferentially absorbed. Good separation of pertechnetate and perrhenate are obtained with perchlorate as the eluent.

VOLATILIZATION. The volatility of technetium heptoxide allows the co-distillation of technetium with acids. Co-distillation from perchloric acid gives good yields, but only a partial separation from rhenium is achieved. Molybdenum is also carried unless complexed by phosphoric acid. Separation from rhenium can be achieved from sulfuric acid, but yields of technetium are can be very poor because of its reduction by trace impurities in the acid. Much more reproducible results can be obtained in the presence of an oxidizing agent, but ruthenium tetroxide (RuO_4) also distills under these conditions. It can be removed, however, by precipitation as ruthenium dioxide RuO_2. In distillation from sulfuric acid-water mixtures, technetium distills in the low-boiling point aqueous fraction, probably as pertechnetic acid. Technetium and rhenium are separated from sulfuric-hydrochloric acid mixtures; pertechnetate is reduced to nonvolatile Tc^{+4} and remains in the acid solution. Technetium heptoxide can be separated from molybdenum trioxide by fractional sublimation at temperatures $\geq$ 300 °C.

ELECTRODEPOSITION. Technetium can be electrodeposited as its dioxide (TcO_2) from 2 M sodium hydroxide. The metal is partially separated from molybdenum and rhenium, but deposition only occurs from low technetium concentrations. Carrier-free ^{95}Tc and ^{96}Tc have been electrolyzed on a platinum electrode from dilute sulfuric acid. Optimum electroplating of technetium has been achieved at pH 5.5 in the presence of very dilute fluoride ion. Yields were better with a copper electrode instead of platinum—about 90 percent was collected in two hours. Yields of 98–99 percent were achieved for platinum electrodes at pH 2-5 when the plating time of up to 20 hours was used. In 2 M sulfuric acid containing traces of fluoride, metallic technetium instead of the dioxide is deposited on the electrode.

Methods of Analysis

Technetium-99 is analyzed by ICP-MS, gas proportional counting, or liquid scintillation from its beta emission. No gamma rays are emitted by this radionuclide. For ICP-MS analysis, technetium is stripped from an extraction chromatography resin and measured by the spectral system. The results should be corrected for interference by ^{99}Ru, if present. For beta analysis, technetium can be electrodeposited on a platinum disc and beta counted. Alternatively, it is collected by extraction-chromatography techniques. The resin from a column or the disc from a filtration system is placed in a liquid scintillation vial and counted. Technetium-99m ($t_{1/2}$=6.0 h), measured by gamma-ray spectrometry, can be used as a tracer for measuring the chemical yield of ^{99}Tc procedures. Conversion electron ejection from the tracer should then be subtracted from the total beta count when measuring ^{99}Tc. Alternatively, samples are counted immediately after isolation and concentration of technetium to determine the chemical recovery, then the ^{99m}Tc is allowed to decay before analysis of the ^{99}Tc. A widely used medical application is the technetium generator. Molybdenum-98 is neutron-irradiated and chemically oxidized to $^{99}MoO_4^{-2}$. This solution is ion-exchanged onto an acid-washed alumina column. After about 1.25 days, the activity of ^{99m}Tc has grown-in to its maximum concentration. The ^{99}Tc is eluted with a 0.9% solution of NaCl, while the ^{99}Mo remains on the column. The column may have its ^{99m}Tc removed after another 1.25 days, but at a slightly smaller concentration. The ^{99m}Tc thus separated is carrier free. This process historically was referred to as “milking,” and the alumina column was called the “cow.”

Neutron activation analysis methods for technetium have been employed since 1972. A method was developed and applied for the analysis of ^{99}Tc in mixed fission products. The method employs chemical separation of ^{99}Tc from most fission products by a cyclohexanone extraction from a basic carbonate solution. Technetium-99 is stripped into water by addition of CCl_4 to the cyclohexanone phase and then isolated on an anion exchange column. Neutron irradiation of the isolated ^{99}Tc was made in the pneumatic facility at a high flux beam reactor (e.g., at a flux of 5×10^{14} n·cm^2/sec for approximately 11 seconds. Thus, after irradiation ^{99}Tc is converted to ^{100}Tc, which, because of its 15.8 second half-life, requires an automatic process to measure its 540 and 591 keV gamma lines.

> Compiled from: Anders, 1960; Bate, 1979; CRC, 1998-99; Choppin et al., 1995; Cobble, 1964; Considine and Considine, 1983; Coomber, 1975; Cotton and Wilkinson, 1988; DOE, 1990 and 1997, 1997; Ehmann and Vance, 1991; Foti et al., 1972a, 1972b; Fried, 1995; Greenwood and Earnshaw, 1984; Hassinsky and Adloff, 1965; Kleinberg et al., 1960; Lindsay, 1988; SCA, 2001; Wahl and Bonner, 1951.

14.10.9.13 Thorium

Thorium, with an atomic number of 90, is the second member in the series of actinide elements. It is one of only three of the actinides—thorium, protactinium, and uranium—that occur in nature in quantities sufficient for practical extraction. In solution, in all minerals, and in virtually all compounds, thorium exists in the +4 oxidation state; it is the only actinide exclusively in the +4 state in solution.

Isotopes

There are 24 isotopes of thorium ranging inclusively from ^{213}Th to ^{236}Th; all are radioactive. Thorium-232, the parent nuclide in the natural decay series, represents virtually 100 percent of the thorium isotopes in nature, but there are ~~a~~ trace amounts of ^{227}Th, ^{228}Th, ^{230}Th, ^{231}Th, and ^{234}Th (progeny of ^{232}Th and $^{235/238}$U). The remaining isotopes are anthropogenic. The most important environmental contaminants are ^{232}Th and ^{230}Th (a member of the ^{238}U decay series). They have half-lives of 1.41×10^{10} years and 75,400 years, respectively.

Occurrence and Uses

Thorium is widely but sparsely dispersed in the Earth’s crust. At an average concentration of approximately 10 ppm, it is over three times as abundant as uranium. In the ocean and rivers, however, its concentration is about one-thousandth that of uranium (about 10^{-8} g/L) because its compounds are much less soluble under environmental conditions. There are six minerals whose essential element is thorium; thorite (uranothorite) and thorianite are common examples. Several lanthanum and zirconium minerals are also thorium-bearing minerals; examples include monazite sand and uraninite. In each mineral, thorium is present as its oxide, thorium dioxide (ThO_2). Monazite sand is the most common commercial mineral, but thorite is also a source of thorium.

Thorium is extracted from its minerals with hot sulfuric acid or hot concentrated alkali, converted into thorium nitrate [$Th(NO_3)_4$] (its chief commercial compound), extracted with organic solvents (commonly kerosene containing tributylphosphate), stripped from the organic phase by alkali solutions, and crystallized as thorium nitrate or precipitated with oxalate. The metal can be produced by electodeposition from the chloride or fluoride dissolved in fused alkali halides or by thermoreduction of thorium compounds by calcium (1,000–1,200 °C). Thorium can also be produced as a by-product in the production of other valuable metals such as nickel, uranium, and zirconium, in addition to the lanthanides. Unextracted minerals or partially extracted mill tailings represent some forms of thorium contaminants found in the environment. Very insoluble forms of thorium hydroxide [$Th(OH)_4$] are other common species found.

Metallic thorium has been used as an alloy in the magnesium industry and as a deoxidant for molybdenum, iron, and other metals. Because of its high density, chemical reactivity, poor mechanical properties, and relatively high cost, it is not used as a structural material. Thorium dioxide is a highly refractory material with the highest melting point among the oxides, 3,390 °C. It has been used in the production of gas mantles, to prevent crystallization of tungsten in filaments, as furnace linings, in nickel alloys to improve corrosion resistance, and as a catalyst in the conversion of methanol to formaldehyde. Thorium-232 is a fuel in breeder reactors. The radionuclide absorbs slow neutrons, and with the consecutive emission of two beta particles, it decays to ^{233}U, a fissionable isotope of uranium with a half-life of 159,000 years.

Solubility of Compounds

Thorium exists in solution as a highly charged ion and undergoes extensive interaction with water and with many anions. Few of the compounds are water soluble; soluble thorium compounds include the nitrate [$Th(NO_3)_4$], sulfate [$Th(SO_4)_2$], chloride ($ThCl_4$), and perchlorate [$Th(ClO_4)_4$]. Many compounds are insoluble in water and are used in the precipitation of thorium from solution, including the hydroxide [$Th(OH)_4$], fluoride (ThF_4), iodate [$Th(IO_3)_4$], oxalate [$Th(C_2O_4)_2$], phosphate [$Th_3(PO_4)_4$], sulfite [$Th(SO_3)_2$], dichromate [$Th(Cr_2O_7)_2$], potassium hexafluorothorionate [K_2ThF_6], thorium ferrocyonide (+2) [$ThFe(CN)_6$], and thorium peroxide sulfate [$Th(OO)_2SO_4$].

The thorium ion forms many complex ions, chelates, and solvated species that are soluble in organic solvents. This property is the basis of many procedures for the separation and purification of thorium (see below). For example, certain ions, such as nitrate and sulfate, form large unsolvated complex ions with thorium that are soluble in organic solvents. Chelates of 1,3-diketones, such as acetylacetone (acac) and TTA, form neutral molecular chelates with the thorium ion that are soluble. In addition, many neutral organic compounds have strong solvating properties for thorium, bonding to the thorium ion in much the same way water solvates the ion at low pH. TBP, diethyl ether, methyl ethyl ketone, mesityl oxide, and monoalkyl and dialkyl phosphates are examples of such compounds.

Review of Properties

Thorium is the first member of the actinide series of elements that includes actinium (Ac), uranium, and the transuranium elements. Thorium is a bright, silver-white metal with a density above 11 g/cm^3. It tarnishes in air, forming a dark gray oxide coating. The massive metal is stable, but in finely divided form and as a thin ribbon it is pyrophoric and forms thorium oxide (ThO_2). Thorium metal dissolves in hydrochloric acid, is made passive by nitric acid, but is not affected by alkali. It is attacked by hot water and steam to form the oxide coating and hydrogen, but its reactions with water are complicated by the presence of oxygen. Thorium has four valence electrons ($6d^27s^2$). Under laboratory conditions, chlorides, bromides, and iodides of the bi- and trivalent state have been prepared. In aqueous solution and in most compounds, including all those found in nature, thorium exists only in the +4 oxidation state; its compounds are colorless in solution unless the anion provides a color. Thorium forms many inorganic compounds in acid solution.

Solution Chemistry

Because the only oxidation state of thorium in solution is the +4 state, its chemistry is not complicated by oxidation-reductions reactions that might produce alternate species in solution. With the +4 charge and corresponding charge-to-radius ratio of 4.0, however, thorium forms very stable complex ions with halides, oxygen-containing ligands, and chelating agents. Although Th^{+4} is large (0.99 Å; 0.099 nm; 99 pm) relative to other +4 ions (Ti, Zr, Hf, Ce) and therefore more resistant to hydrolysis, as a highly charged ion, it hydrolyzes extensively in aqueous solutions above pH 3 and tends to behave more like a colloid than a true solution. The concentration of Th^{+4} is negligible under those conditions. Below pH 3, however, the uncomplexed ion is stable as the hydrated ion, $Th(H_2O)_{8\text{ or }9}{}^{+4}$.

COMPLEXATION. Thorium has a strong tendency to form complex ions in solution. The presence of HF forms very stable complex ions, for example, with one, two, or three ligands:

$$Th^{+4} + HF \rightarrow ThF^{+3} + H^{+1}$$
$$ThF^{+3} + HF \rightarrow ThF_2{}^{+2} + H^{+1}$$
$$ThF_2{}^{+2} + HF \rightarrow ThF_3{}^{+1} + H^{+1}$$

These complex ions represent the predominant species in solutions containing HF. Stable complex ions also form with oxygen-containing ligands such as nitrate, chlorate, sulfate, bisulfate, iodate, carbonate, phosphate, most carboxylate anions, and chelate anions. Some chelating agents such as salicylate, acetylacetonate (acac), TTA, and cupferron form complexes that are more soluble in organic solvents, This property is the basis of several radiochemical isolation methods for thorium. Through the formation of soluble complex ions, chelating agents found in some industrial wastewater or natural water samples will interfere to varying degrees with the isolation of thorium by ferric hydroxide [$Fe(OH)_3$] coprecipitation. Alternative isolation methods should be used, such as coprecipitation from an acidic solution with an alternative reagent. Protonation of the anionic form of chelates with acid renders them useless as chelating agents. Other complexing agents also interfere with precipitation by the formation of soluble ions. Thorium, for example, does not precipitate with oxalate in the presence of carbonate ions. A procedure for separating thorium from rare-earth ions takes advantage of the formation of a soluble thorium-EDTA complex that inhibits thorium precipitation when the rare-earth ions are precipitated with phosphate. The presence of high concentrations of other complexing agents such as phosphate, chloride, and other anions found in some samples takes thorium into a completely exchangeable form when it is solubilized in high-concentration nitric acid.

HYDROLYSIS. Beginning at pH 3, thorium ions undergo extensive hydrolysis to form monomeric and polymeric complexes in solution, leaving little Th^{+4} in a saturated solution at pH 3 (approximately 5×10^{-6} M). Tracer solutions containing ^{234}Th can be added at pH 2 to allow equilibration because it is not likely to occur if part of the thorium is hydrolyzed and bound in polymeric forms.

The hydrolysis process is complex, depending on the pH of the solution and its ionic strength. Several species have been proposed: three are polynuclear species, $Th_2(OH)_2^{+6}$, $Th_4(OH)_8^{+8}$, and $Th_6(OH)_{15}^{+9}$; and two are monomeric species, $Th(OH)^{+3}$ and $Th(OH)_2^{+2}$. The monomeric species are of minor importance except in extremely dilute solutions, but they become more important as the temperature increases. The presence of chloride and nitrate ion diminishes hydrolysis, because the formation of corresponding complex ions markedly suppresses the process. Hydrolysis increases with increasing hydroxide concentration (pH), and eventually polymerization of the species begins. At a pH of about 5, irreversible hydrolysis produces an amorphous precipitate of thorium hydroxide, a polymer that might contain more than 100 thorium atoms. Just before precipitation, polymerization slows and equilibration might take weeks or months to obtain.

Routine fuming of a sample containing organic material with nitric acid is recommended after addition of tracer, but before separation of thorium as a hydroxide precipitate because there is evidence for lack of exchange between added tracer and isotope already in solution. Complexing with organic substances in the initial solution or existence of thorium in solution as some polymeric ion have been suggested as the cause.

ADSORPTION. The insoluble hydroxide that forms in solution above pH 3 has a tendency to coagulate with hydrated oxides such as ferric oxide. The high charge of the Th^{+4}cation, high charge-to-radius ratio, and tendency to hydrolyze all contribute to the ability of thorium to adsorb on surfaces by ion-exchange mechanisms or chemical adsorption mechanisms. These adsorption properties greatly affect the interaction of thorium with ion-exchange resins and environmental media such as soil.

Dissolution of Samples

Thorium samples are ignited first to remove organic materials. Most compounds will decompose when sintered with sodium peroxide (Na_2O_2), and most thorium minerals will yield to alternate sodium peroxide sintering and potassium pyrosulfate ($K_2S_2O_7$) fusion. It is often necessary to recover thorium from hydrolysis products produced by these processes. The hydrolysis products are treated with hydrofluoric acid, and thorium is recovered as the insoluble fluoride. Rock samples are often dissolved in hydrofluoric acid containing either nitric acid or perchloric acid. Monazite is dissolved by prolonged sintering or with fuming perchloric or sulfuric acid. Thorium alloys are dissolved in two steps, first with aqua regia (nitric and hydrochloric acid mixture) followed by fusion with potassium pyrosulfate. Thorium targets are dissolved in concentrated nitric acid containing hydrofluoric acid, mantles in nitric or sulfuric acid, and tungsten filaments with aqua regia or perchloric acid.

Separation Methods

PRECIPITATION AND COPRECIPITATION. Precipitation and coprecipitation are used to separate and collect thorium from aqueous solutions either for further treatment in an analytical scheme or for preparation of a sample for counting. Formation of insoluble salts is used to precipitate thorium from solution; examples include the hydroxide, peroxide, fluoride, iodate, oxalate, and phosphate, among others. Tracer quantities of thorium are commonly coprecipitated with lanthanum fluoride (LaF_3), neodymium fluoride (NdF_3), and cerium fluoride (CeF_3) in separation schemes and to prepare samples for alpha counting. Tracer quantities are also carried with calcium oxalate [$Ca(C_2O_4)$], ferric hydroxide [$Fe(OH)_3$], zirconium iodate [$Zr(IO_3)_4$], zirconium phosphate [$Zr_3(PO_4)_4$], and barium sulfate ($BaSO_4$).

ION EXCHANGE. The highly charged thorium cation is strongly adsorbed onto cation exchangers and is more difficult to elute than most other ions. Its strong adsorption property makes it possible to remove trace quantities of thorium from a large volume of solution onto small amounts of ion-exchange resin. Washing the resin with mineral acids of various concentrations separates thorium from less strongly bound cations that elute from the resin. For example, Th^{+4} remains bonded at all hydrochloric concentrations, allowing other cations to be eluted at different concentrations of acid. Thorium is eluted by complexing agents such as citrate, lactate, fluoride, carbonate, sulfate, or oxalate that reduce the net charge of the absorbing species, causing reversal of the adsorption process.

Anion exchangers are useful for separating thorium, but the contrasting behavior of thorium with the resin depends on whether hydrochloric or nitric acid is used as an eluent. In hydrochloric acid, several metal ions, unlike thorium, form negative complexes that can be readily removed from a thorium solution by adsorption onto the anionic exchanger. Thorium forms positively charged chlorocation complexes or neutral thorium chloride ($ThCl_4$) in the acid and is not exchanged onto the resin at any hydrochloric acid concentration. In contrast, thorium forms anionic complexes in nitric acid solution that adsorb onto the exchanger over a wide range of nitric acid concentrations, reaching a maximum affinity near 7 M nitric acid. Behavior in nitric acid solution is the basis for a number of important radiochemical separations of thorium from rare earths, uranium, and other elements.

ELECTRODEPOSITION. Thorium separated from other actinides by chemical methods can be electrodeposited for alpha counting from a dilute solution of ammonium sulfate adjusted to a pH of 2. The hydrous oxide of thorium is deposited in one hour on a highly polished platinum or stainless-steel disc serving as the cathode of an electrolytic cell. The anode is a platinum-iridium alloy.

SOLVENT EXTRACTION. Many complexes and some compounds of thorium can be extracted from aqueous solutions into a variety of organic solvents. The TTA (α-theonyltrifluoroacetone) complex of metals is widely used in radiochemistry for the separation of ions. Thorium can be separated from most alkali metal, alkaline earth, and rare earth metals after the complex is quantitatively extracted into benzene above pH 1. Backwashing the organic solution with dilute acid leaves the more soluble ions in benzene.

Extraction of nitrates and chlorides of thorium into organic solvents from the respective acid solutions is widely used for isolation and purification of the element. One of the most common processes is the extraction of thorium nitrate from a nitric acid solution with TBP. TBP is usually diluted with an inert solvent such as ether or xylene/toluene to reduce the viscosity of the mixture. Dilution reduces the extraction effectiveness of the mixture, but the solubility of many contaminating ions is greatly reduced, increasing the effectiveness of the separation when the thorium is recovered by backwashing.

Long-chain amine salts have been very effective in carrying thorium in laboratory and industrial extraction process using xylene/toluene. Complex sulfate anions of thorium are formed in sulfuric acid that act as the counter ion to the protonated quaternary amine cation. They accompany the organic salt into the organic phase.

In recent years, solvent extraction chromatography procedures have been developed to separate thorium. These procedures use extraction chromatography resins that consist of extractant materials such as Aliquat-336® (tricaprylylmethylammonium chloride or methyltricaprylyl-ammonium chloride), CMPO in TBP, or DPPP (dipentylpentylphosphonate), also called DAAP (diamylamylphosphonate), or absorbed onto an inert polymeric material. They are used in a column, rather than in the traditional batch mode, and provide a rapid efficient method of separating the radionuclide with the elimination of large volumes of organic waste.

Methods of Analysis

Chemical procedures are used for the analysis of macroscopic quantities of thorium in solution after it has been separated by precipitation, ion exchange, extraction, and/or extraction chromatography from interfering ions. Gravimetric determination generally follows precipitation as the oxalate that is calcined to the oxide (ThO_2). Numerous volumetric analyses employ EDTA as the titrant. In the most common spectrometric method of analysis, thorin, a complex organoarsenic acid forms a colored complex with thorium that is measured in the visible spectrum.

Trace quantities of thorium are measured by alpha spectrometry after chemical separation from interfering radionuclides. Thorium-227, ^{228}Th, ^{230}Th, and ^{232}Th are determined by the measurement of their respective spectral peaks (energies), using ^{234}Th as a tracer to determine the chemical yield of the procedure. The activity of the tracer is determined by beta counting in a proportional counter. Thorium-234 also emits gamma radiation that can be detected by gamma spectrometry; however, the peak can not be measured accurately because of interfering peaks of other gamma-emitting radionuclides. Thorium-229 is sometimes used as a tracer to determine the chemical yield of the alpha spectrometric procedure, but it produces considerable recoil that might contaminate the detector.

> Compiled from: Ahrland, 1986; Baes and Mesmer, 1976; Cotton, 1991; Cotton and Wilkinson, 1988; DOE, 1990 and 1997, 1997; EPA, 1980 and 1984; Greenwood, 1984; Grimaldi, 1961; Hassinsky and Adloff, 1965; Hyde, 1960; Katzin, 1986; Lindsey, 1988.

14.10.9.14 Tritium

Unlike the elements reviewed in this section, tritium is the only radionuclide of the element hydrogen. It contains two neutrons and is represented by the symbols ^{3}H, ^{3}T, or simply, T. The atom contains only one valence electron so its common oxidation state, besides zero, is +1, although it can exist in the -1 state as a metal hydride.

Occurrence and Uses

Tritium is found wherever hydrogen is found, with and without the other isotopes of the element (hydrogen and deuterium)—as molecular hydrogen (HT, DT, T_2), water (HOT, DTO, T_2O), and inorganic and organic compounds, hydrides and hydrocarbons, respectively, for example. About 99 percent of the radionuclide in nature from any source is in the form of HOT. Natural processes account for approximately one T atom per 10^{18} hydrogen atoms. The source of some natural tritium is ejection from the sun, but the primary source is from bombardment of ^{14}N with cosmic neutrons in the upper atmosphere:

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \rightarrow ^{3}\mathrm{H} + ^{12}_{6}\mathrm{C}$$

Most tritium from this source appears as HOT.

Tritium is produced in laboratory and industrial processes by nuclear reactions such as:

$$^{2}_{1}\mathrm{D} + ^{2}_{1}\mathrm{D} \rightarrow ^{3}_{1}\mathrm{T} + ^{1}_{1}\mathrm{H}$$

For large-scale production of tritium, ^{6}Li alloyed with magnesium or aluminum is the target of neutrons:

$$^{6}_{3}\mathrm{Li} + ^{1}_{0}\mathrm{n} \rightarrow ^{3}_{1}\mathrm{T} + ^{4}_{2}\mathrm{He}$$

The radionuclide is retained in the alloy until released by acid dissolution of the target. Large quantities are handled as HT or HOT. HOT is formed from HT when it is exposed to oxygen or water vapor. A convenient way to store tritium is as the hydride of uranium (UT_3). It is formed by reacting the gas with finely divided uranium and is released by heating the compound above 400 °C.

Tritium is also produced in nuclear reactors that contain water or heavy water from the neutron bombardment of boron, lithium, and deuterium:

$$^{10}\mathrm{B(n, T)}\ 2\ ^{4}\mathrm{He}$$
$$^{11}\mathrm{B(n, T)}\ ^{9}\mathrm{Be}$$
$$^{6}\mathrm{Li\ (n, T)}\ ^{4}\mathrm{He}$$
$$^{2}\mathrm{H\ (n,}\gamma\mathrm{)\ T}$$

and from the fission process as a ternary fission fragment. Significant uses for tritium are in fission bombs to boost their yield, in thermonuclear weapons (the hydrogen bomb), in luminescent signs, and in night-vision military applications. Tritium bombarded with high-energy deuterons undergoes fusion to form helium and releases neutrons:

$$^{3}_{1}\mathrm{H} + ^{2}_{1}\mathrm{H} \rightarrow ^{4}_{2}\mathrm{He} + ^{1}_{0}\mathrm{n}$$

A tremendous amount of energy is released during the nuclear reaction, much more than the energy of the bombarding particle. Fusion research on controlled thermonuclear reactions should lead to an energy source for electrical generation.

Tritium absorbed on metals are a source of neutrons when bombarded with deuterons. Mixed with zinc sulfide, it produces radioluminescence that is used in luminescent paint and on watch dials. Gaseous tritium in the presence of zinc sulfide produces a small, permanent light source found in rifle sights and exit signs. Tritium is also a good tracer because it does not emit gamma radiation. Hydrological studies with HOT are used to trace geological water and the movement of glaciers. It is also used as a tracer for hydrogen in chemical studies and biological research. In medicine, it is used for diagnosis and radiotreatment.

Review of Properties

Tritium ($t_{½} \approx 12.3$ y) decays by emission of a low-energy beta particle to form ^{3}He, and no gamma radiation is released. The range of the beta particle is low, 6 mm in air and 0.005 mm in water or soft tissue.

The physical and chemical properties of tritium are somewhat different than hydrogen or deuterium because of their mass differences (isotope effects). Tritium is approximately 1.5 times as heavy as deuterium and three times heavier than hydrogen, and the isotope effect can be large for mass differences of these magnitudes. In its simple molecular form, tritium exists primarily as T_2 or DT. The oxide form is HOT, DTO, or T_2O, with higher molecular weights than water (H_2O). Thus molecules of tritiated water are heavier, and any process such as evaporation or distillation that produces a phase transition results in isotopic fractionation and enrichment of tritium in water. In a mixture of the oxides, various mixed isotopic water species are generally also present because of exchange reactions: in any mixture of H_2O, D_2O, and T_2O, HOT and DTO are found.

Tritium can be introduced into organic compounds by exposing T_2 to the compound for a few days or weeks, irradiation of the compound and a lithium salt with neutrons (recoil labeling), or it can be selectively introduced into a molecule by chemical synthesis using a molecular tritium source such as HOT. Beta radiation causes exchange reactions between hydrogen atoms in the compound and tritium and migration of the isotope within the molecule. Phenol (C_6H_5OH), for example, labeled with tritium on the oxygen atom (C_6H_5OT) will become C_6H_4TOH and C_6H_4TOT. When tritium samples are stored in containers made from organic polymers such as polyethylene, the container will adsorb tritium, resulting in a decrease in the concentration of tritium in the sample. Eventually, the tritium atoms will migrate to the outer surface of the container, and tritium will be lost to the environment. Catalytic exchange also occurs in tritiated solutions or solutions containing T_2 gas. Exchange is very rapid with organic compounds when H^{+1} or OH^{-1} ions or if a hydrogen-transfer agent such as Pt or Pd is present.

Tritium as HT or HOT will absorb on most metallic surfaces. Penetration at room temperature is very slow, and the radionuclide remains close to the surface. In the form of HOT, it can be removed with water, or by hydrogen gas in the form of HT. Heating aids the removal. When tritium is absorbed at elevated temperatures, it penetrates deeper into the surface. Adsorption under these conditions will result in enough penetration to cause structural damage to the metal, especially if the process continues for extended periods. Hydrogenous material such as rubber and plastics will also absorb tritium. It will penetrate into the material, and hydrogenous materials are readily contaminated deep into the material, and it is impossible to completely remove the tritium. Highly contaminated metal or plastic surfaces can release some of the loosely bound tritium immediately after exposure in a process called outgassing.

Pure T_2O can be prepared by oxidation of tritium gas with hot copper oxide (Cu^{+2}) or direct combination of the gas with oxygen in the presence of an electrical spark. It is never used for chemical or biological processes because one milliliter contains 2,650 curies. The liquid is self-luminescent, undergoes rapid self-radiolysis, and considerable radiation damage is done to dissolved species. For the same reason, very few compounds of pure tritium have ever been prepared or studied.

Tritium is not a hazard outside the body. Gamma radiation is not released by its decay. The beta emission is low in energy compared to most beta emitters and readily stopped by the outer layer of skin. Only ingested tritium can be a hazard. Exposure to tritium is primarily in the form of HT gas or HOT water vapor, although T_2 and T_2O may be present. Only about 0.005 percent of the activity of inhaled HT gas is incorporated into lung tissue, and most is exhaled. In addition, tritiated water can be absorbed through the skin or wounds unless protective equipment is used. Tritium is found in tissue wherever hydrogen is found. The biological half-life is about ten days, but the value varies significantly, depending on exertion rates and fluid intake.

Environmental tritium is formed in the gaseous and aqueous forms, but over 99 percent of tritium from all sources is found in the environment after exchange with hydrogen in water in the form of HOT. It is widely distributed in the surface waters of the Earth and makes a minor contribution to the activity of ocean water. It can also be found in laboratories and industrial sites in the form of metal hydrides, tritiated pump oil, and tritiated gases such as methane and ammonia.

Tritium found in environmental samples may be either exchangeable in acid media (labile) or organically bound. In the latter case, combustion of the material is necessary to release the tritium into an exchangeable form. This is performed usually by adding an oxidizing agent, like $KMnO_4$, if the contribution of the organic tritium to the total tritium is large.

Separation Methods

DISTILLATION. Tritium in water samples is essentially in the form of HOT. It can be removed quantitatively from aqueous mixtures by distillation to dryness, which also separate it from other radionuclides. Volatile iodine radionuclides are precipitated as silver iodide before distillation, if they are present. The aqueous solution is usually distilled, however, from a basic solution of potassium permanganate, which will oxidize radionuclides, such as iodine and carbon, and oxidize organic compounds that might interfere with subsequent procedures, liquid scintillation counting, for example. Charcoal can also be added to the distillation mixture as an additional measure to remove organic material. Contaminating tritium in soil samples can be removed by distillation from similar aqueous mixtures. All tritium in soil samples might not be recovered by this method, however, if the tritium is tightly bound to the soil matrix. Tritium also can be removed by distillation of an azeotrope mixture formed with toluene or cyclohexane. In some procedures, tritium is initially separated by distillation and then concentrated (enriched) by electrolysis in an acid or base solution. Recovery of tritium from the electrolytic cell for analysis is accomplished by a subsequent distillation.

DECOMPOSITION. Organically bound tritium in vegetation, food, and tissue samples can be removed by combustion. The sample is freeze dried (lyophilized), and the water from the process is collected in cold traps for tritium analysis. The remaining solid is collected as a pellet, which is burned at 700 °C in a highly purified mixture of argon and oxygen in the presence of a copper(I) oxide (Cu_2O) catalyst, generated on a copper screen at the temperature of the process. Water from the combustion process, containing tritium from the pellet, and water from the freeze-drying process is analyzed for tritium by liquid scintillation counting.

Tritium in HOT can be reduced to TH by heating with metals, such as magnesium, zinc, or calcium, and analyzed as a gas. Conversely, if tritium is present as HT or T_2, it may be oxidized to HOT by passing the gaseous sample over a platinum, palladium, or nickel catalyst in the presence of air.

CONVERSION TO ORGANIC COMPOUNDS. Compounds that react readily with water to produce hydrogen derivatives can be used to isolate and recover tritium that is present in the HOT form. Organic compounds containing magnesium (Grignard reagents) with relatively low molecular-weights will react spontaneously with water and produce a gaseous product containing hydrogen from the water. Tritium from HOT in a water sample will be included in the gaseous sample. It is collected after formation by condensation in a cold trap and vaporized into a gas tube for measurement. Grignard reagents formed from butane, acetylene, and methane can be used in this method. Tritiated butane is produced by the following chemical reaction:

$$C_4H_9MgBr + THO \rightarrow C_4H_9T + Mg(OH)Br$$

Inorganic compounds can also be use to produce gaseous products:

$$Al_4C_3 + 3\ HOT + 9\ H_2O \rightarrow 3\ CH_3T + 4\ Al(OH)_3$$

EXCHANGE. Methods to assess tritium in compounds take advantage of exchange reactions to collect the radionuclide in a volatile substance that can be collected in a gas tube for measurement. Acetone is one compound that easily exchanges tritium in an acid or base medium and is relatively volatile.

Methods of Analysis

Tritium is collected primarily as HOT along with water (H_2O) by distillation and then determined from its beta emission in a liquid scintillation system. No gamma rays are emitted. The distillation process is usually performed from a basic solution of potassium permangenate to oxidize radionuclides and organic compounds, preventing them from distilling over and subsequently interfering with counting. Charcoal can also be added to the distillation mixture as an additional measure to remove organic material. Volatile iodine radionuclides can be precipitated as silver iodide before distillation. Another distillation technique involves the use of cyclohexane to form an azeotropic (low boiling point) mixture. This technique is sometimes used in analysis of biota samples. Tritium may be analyzed, indirectly, by mass spectrometry of its progeny, ^{3}He.

> Compiled from: Choppin et al., 1995; Cotton and Wilkinson, 1988; DOE, 1994; Demange et al., 2002; Duckworth, 1995; Greenwood and Earnshaw, 1984; Hampel, 1968; Hassinky and Adloff, 1965; Kaplan, 1995; Lindsay, 1988; Mitchell, 1961; Passo and Cook, 1994; Surano et al., 1992.

14.10.9.15 Uranium

Uranium, atomic number 92, is the last naturally occurring member of the actinide series and the precursor to the transuranic elements. Three isotopes are found in nature, and uranium was the active constituent in the salts whose study led to the discovery of radioactivity by Becquerel in 1896.

Isotopes

There are 19 isotopes of uranium with mass numbers ranging from 222 to 242. All isotopes are radioactive with half-lives range ranging from microseconds to billions of years. Uranium-235 (0.72%) and ^{238}U (99.27%) occur naturally as primordial uranium. Uranium-234 has a natural abundance of 0.0055%, but is present as a part of the ^{238}U decay natural decay chain. The ^{234}U that was formed at the time the Earth was formed has long since decayed. The half-lives of these principal isotopes of uranium are listed below.

Isotope	Alpha Decay Half-Life	Spontaneous Fission Half-Life
234	2.46×10^5 years	1.42×10^{16} years
235	7.04×10^8 years	9.80×10^{18} years
238	4.48×10^9 years	8.08×10^{15} years

These isotopes have two different decay modes. Each decay mode has its own characteristic half-life. As seen above the alpha decay mode is the most significant, because it has the shortest half-life for each of these isotopes.

Another isotope of uranium of significance is ^{232}U ($t_{½}$ ≈ 69.8 y). It is used as a tracer in uranium analyses and is also an alpha emitter so it can be determined concurrently with the major uranium isotopes by alpha spectrometry.

Uranium-235 and artificially produced ^{233}U are fissionable material on bombardment with slow (thermal) neutrons. Other uranium radionuclides are fissionable with fast moving neutrons, charged particles, high-energy photons, or mesons. Uranium-238 and ^{235}U are both parents of natural radioactive decay series, the uranium series of ^{238}U that eventually decays with alpha and beta emissions to stable ^{206}Pb and the actinium series of ^{235}U that decays to ^{207}Pb.

Occurrence and Uses

Naturally occurring uranium is believed to be concentrated in the Earth's crust with an average concentration of approximately 4 ppm. Granite rocks contains up to 8 ppm or more, and ocean water contains 0.0033 ppm. Many uranium minerals have been discovered. Among the better known are uraninite, carnotite, adavidite, pitchblende, and coffinite. The latter two minerals are important commercial sources of uranium. It is also found in phosphate rock, lignite, and monazite sands and is commercially available from these sources. The artificial isotope, ^{233}U, is produced from natural ^{232}Th by absorption of slow neutrons to form ^{233}Th, which decays by the emission of two beta particles to ^{233}U.

Uranium is extracted from uranium minerals, ores, rocks, and sands by numerous chemical extraction (leaching) processes. The extraction process is sometimes preceded by roasting the ore to improve the processing characteristic of the material. The extraction process uses either an acid/oxidant combination or sodium carbonate treatment, depending on the nature of the ore, to convert the metal to a soluble form of the uranyl ion. Uranium is recovered from solution by precipitating the uranate salt with ammonia or sodium hydroxide solution. Ammonium uranate is known as "yellow cake." The uranate salt is solubilized to give a uranyl nitrate solution that is further purified by extraction into an organic phase to separate the salt from impurities and subsequent stripping with water. It is precipitated as a highly purified nitrate salt that is used to produce other uranium compounds—uranium trioxide (UO_3) by thermal processing or uranium dioxide (UO_2) on reduction of the trioxide with hydrogen. Uranium tetrafluoride (UF_4) is prepared, in turn, from the dioxide by treatment with hydrogen fluoride. The metal is recovered by fused-salt electrolysis in molten sodium chloride-calcium chloride or reduction with more active metals such as calcium or magnesium (Ames Process) in an inert atmosphere at 1,000 °C.

Early in the twentieth century, the only use of uranium was in the production of a brown-yellow tinted glass and glazes; it was a byproduct of the extraction of radium, which was used for medicinal and research purposes. Since the mid-twentieth century, the most important use of uranium is as a nuclear fuel, directly in the form of ^{233}U and ^{235}U, fissionable radionuclides, and in the form of ^{238}U that can be converted to fissionable ^{239}Pu by thermal neutrons in breeder reactors. Depleted uranium, uranium whose ^{235}U content has been reduced to below about 0.2

percent, the majority of waste from the uranium enrichment process, is used in shielded containers to transport radioactive materials, inertial guidance devices, gyro compasses, counterweights for aircraft control surfaces, ballast for missile reentry vehicles, fabrication of armor-piercing conventional weapons, and tank armor plating. Uranium metal is used as a X-ray target for production of high-energy X-rays, the nitrate salt as a photographic toner, and the acetate is used in analytical chemistry.

Solubility of Compounds

Only a small number of the numerous uranium compounds are soluble in water. Except for the fluorides, the halides of uranium (+3 and +4) are soluble, as are the chloride and bromide of U(V) [UOX_2] and the fluoride, chloride, and bromide of U(VI) [UO_2X_2]. Several of the uranyl (UO_{2+2}) salts of polyatomic anions are also soluble in water: the sulfate, bicarbonate, acetate, thiocyanate, chromate, tungstate, and nitrate. The latter is one of the most water-soluble uranium compounds.

Review of Properties

Uranium is a dense, malleable and ductile metal that exists in three allotropic forms: alpha, stable to 688 °C where it forms the beta structure, which becomes the gamma structure at 776 °C. It is a poor conductor of electricity. The metal absorbs gases and is used to absorb tritium. Uranium metal tarnishes readily in an oxidation process when exposed to air. It burns when heated to 170 °C, and the finely divided metal is pyrophoric. Uranium slowly decomposes water at room temperature, but rapidly at 100 °C. Under a flux of neutrons and other accelerated particles, atoms of uranium are displaced from their equilibrium position in its metallic lattice. With high temperatures and an accumulation of fission products, the metal deforms and swells, becoming twisted, porous, and brittle. The problem can be avoided by using some of its alloys, particularly alloys of molybdenum and aluminum.

Uranium forms a large number of binary and ternary alloys with most metals. It also forms compounds with many metals: aluminum, bismuth, cadmium, cobalt, gallium, germanium, gold, indium, iron, lead, magnesium, mercury, nickel, tin, titanium, zinc, and zirconium. Many binary compounds of the nonmetals are also known: hydrides, borides, carbides, nitrides, silicides, phosphides, halides, and oxides. Although other oxides are known, the common oxides are UO_2, UO_3, and U_3O_8. Uranium reacts with acids to form the +4 salts and hydrogen. It is very reactive as a strong reducing agent.

Uranium compounds are toxic at high concentrations. The physiological damage occurs to internal organs, especially the kidneys. The radioactivity of natural uranium radionuclides is not of great concern, although it is high for some artificial isotopes. Natural uranium in the environment is considered a relatively low hazard, however, because of its very long half-life and low toxicity at minute concentrations.

Uranium in nature is almost entirely in the +4 and VI oxidation states. It occurs as the oxides, UO_2 and U_3O_8, in the solid state. In ground water under oxic conditions it exists as UO_2^{+2} or complexes of carbonate such as $UO_2(CO_3)_3^{-4}$. Complex formation increases its solubility under all conditions in normal groundwater and even under fairly strong reducing conditions. The amount associated with particulate matter is small in natural oxic waters. In some waters, solubility may be limited, however, by formation of an uranyl silicate species. Uranium in general is poorly absorbed on geologic media under oxic conditions, especially at moderate and high concentrations and in the presence of high carbonate concentrations. A significant adsorption occurs at pH above about 5 or 6 because of formation of hydrolytic complexes. Reduction to the IV oxidation state would increase uptake in the environmental pH range.

Solution Chemistry

The radiochemistry of uranium is complicated because of the multiple oxidation states that can exist in solution and the extensive complexation and hydrolytic reactions the ions are capable of undergoing in solution. Four oxidation states are possible: +3, +4, (V) and (VI); the latter two exist as oxycations: UO_2^{+1} and UO_2^{+2}, respectively. Their stabilities vary considerably, and the +4 and +6 states are stable in solution under certain conditions; oxidation-reduction reagents are used to form and maintain these ions in solution. Each ion has different chemical properties, and those of the +4 and (VI) states have been particularly exploited to stabilize, solubilize, separate, and collect uranium. The multiple possibilities of oxidation state, complexation, and hydrolysis should be carefully considered when planning any radiochemical procedures.

OXIDATION-REDUCTION BEHAVIOR. The multiple oxidation states can be exploited during separation procedures by taking advantage of their different chemical properties. Thorium can be separated from uranium, for example, by oxidizing uranium in solution to the +6 oxidation state with 30 percent hydrogen peroxide (H_2O_2) and precipitating thorium as the hydroxide; in the +6 state, uranium is not precipitated.

The U^{+3} ion is an unstable form of uranium, produced in perchlorate or chloride solutions by reduction of UO_2^{+2} electrochemically or with zinc amalgam. It is a powerful reducing agent, and is oxidized to U^{+4} by chlorine or bromine. U^{+3} is slowly oxidized by water with the release of hydrogen, and oxygen from air causes rapid oxidation. Aqueous solutions are red-brown and are stable for several days in 1 M hydrochloric acid, especially if kept cold; rapid oxidation occurs in more concentrated acid solutions.

The tetrapositive uranous ion, U^{+4}, is produced by dissolving water-soluble salts of the ion in solution, dissolving uranium metal with sulfuric or phosphoric acid, reduction of UO_2^{+1} during its disproportionation reaction, reduction of UO_2^{+2} by Cr^{+2} or Ti^{+3}, or oxidation of U^{+3}. The tetrapositive ion is green in solution. The ion is stable, but slowly oxidizes by oxygen from air to the +6 state.

The UO_2^{+1} ion (V) is extremely unstable in solution and exist only as a transient species, disproportionating rapidly to U^{+4} and UO_2^{+2} according to the following reaction in the absence of complicating factors ($k = 1.7 \times 10^6$):

$$2\ UO_2^{+1} + 4\ H^{+1} \rightleftharpoons UO_2^{+2} + U^{+4} + 2\ H_2O$$

Maximum stability is observed in the pH range 2–4 where the reaction is considerably slower. Solutions of UO_2^{+1} are prepared by the dissolution of UCl_5 or reduction of UO_2^{+2} ions electrochemically or with U^{+4} ions, hydrogen, or zinc amalgam.

Uranium(VI) is generally agreed to be in the form of the dioxo or uranyl ion, UO_2^{+2}. As the only oxidation state stable in contact with air, it is very stable in solution and difficult to reduce. Because of its exceptional stability, the uranyl ion plays a central role in the radiochemistry of uranium. It is prepared in solution by the dissolution of certain water-soluble salts: nitrate, halides, sulfate, acetate, and carboxylates; by dissolution of uranium(VI) compounds; and oxidation of lower-oxidation state ions already in solution, U^{+4} with nitric acid for example. Its solutions are yellow in color.

COMPLEXATION. Uranium ions form numerous complex ions, and the solution chemistry of uranium is particularly sensitive to complexing agents present. Complex-ion chemistry is very important, therefore, to the radiochemical separation and determination of uranium. Complexation, for example, provides a method to prevent the removal of uranium ions or its contaminants from solution and can influence the stability of ions in solution.

Among the oxidation states exhibited in solution, the tendency for formation of anionic complexes is:

$$U^{+4} > UO_2^{+2} > U^{+3} > UO_2^{+1},$$

while the order of stability of the anionic complexes is represented by:

fluoride > nitrate > chloride > bromide > iodide > perchlorate > carbonate > oxalate > sulfate.

Numerous organic complexes form, including citrate, tartrate, and EDTA, especially with UO_2^{+2}.

There is evidence for only a few complexes of U^{+3}, cupferron and chloride for example. In contrast, tetrapositive uranium, U^{+4}, forms complexes with a wide variety of anions, and many are stable: halides—including fluoride (up to eight ligands, UF_8^{-4})—chloride, and bromide; thiocyanate; and oxygen-donors, nitrate, sulfates, phosphates, carbonate, perchlorate, and numerous carboxylates: acetate, oxalate, tartrate, citrate, and lactate. The low charge on UO_2^{+1} precludes the formation of very stable complexes. Fluoride (from hydrogen fluoride) is notable, however, in its ability to displace oxygen from the ion, forming UF_6^{-1}—which inhibits disproportionation—and precipitating the complex ion from aqueous solution. The uranyl ion, UO_2^{+2}, readily forms stable complexes with a large variety of inorganic and carboxylate anions very similar to those that complex with U^{+4}. In addition, numerous organic ligands besides carboxylates are known that contain both oxygen and nitrogen as donor atoms. Complex-ion formation must be considered, therefore, during precipitation procedures. Precipitation of uranium ions is inhibited, for example, in solutions containing carbonate, tartrate, malate, citrate, hydroxylamine, while impurities are precipitated as hydroxides, sulfides, or phosphates. Conversely, uranium is precipitated with ammonia, while other ions are kept in solution as complexes of EDTA.

HYDROLYSIS. Some uranium ions undergo extensive hydrolysis in aqueous solution. The reactions can lead to formation of polymeric products, which form precipitates under certain conditions. The tendency of the various oxidation states toward hydrolysis, a specific case of complexation, is, therefore, in the same order as that of complex-ion formation (above).

Little data are available on the hydrolysis of U^{+3} ion because it is so unstable in solution. Qualitative evidence indicates, however, that hydrolysis is about that expected for a +3 ion of its size—a much weaker acid than most other metals ions of this charge. The U^{+4} ion is readily hydrolyzed in solution, but exists as the unhydrolyzed, hydrated ion in strongly acidic solutions. Hydrolysis begins at pH<1, starting with the $U(OH)^{+3}$ species. As pH increases, several species form progressively up to $U(OH)_5^{-1}$. The $U(OH)^{+3}$ species predominates at high acidity and low uranium concentrations, and the concentration of each species increases rapidly with the temperature of the solution. In less acidic solutions and as the concentration of uranium increases, a polymeric species forms, probably $U_6(OH)_{15}^{+9}$. Hydrolytic complexes of high molecular weight probably form subsequently, culminating in precipitation. Hydrolysis of the UO_2^{+1} ion has been estimated to be very low, consistent with the properties of a large, positive ion with a single charge. Hydrolysis of UO_2^{+2} begins at about pH 3 and is fairly complicated. In very dilute solutions, the monomeric species, $UO_2(OH)^{+1}$, forms initially; but the dimerized species, $(UO_2)_2(OH)_2^{+2}$, rapidly becomes the dominant form in solution, existing in a wide range of uranium concentration and pH. As the pH increases, more complex polynuclear species become prominent. The presence of complexing agents, such as chloride, nitrate, and sulfate ions suppress hydrolysis to varying degrees.

Dissolution of Samples

Metallic uranium dissolves in nitric acid to form uranyl nitrate. Large amounts dissolve moderately rapidly, but fine turnings or powder may react violently with nitric acid vapors or nitrogen dioxide in the vapor. The presence of oxygen in the dissolution system tends to reduce the oxides. The rate of dissolution of large amounts of uranium may be increased by the addition of small amounts of sulfuric, phosphoric, or perchloric acids to the nitric acid solution. Other common mineral acids such as sulfuric, phosphoric, perchloric, hydrochloric, and hydrobromic acid are also used to dissolve uranium metal. Simple organic acids in hydrochloric acid dissolve the metal, and other solvent systems are used: sodium hydroxide and hydrogen peroxide, bromine in ethyl acetate, and hydrogen chloride in ethyl acetate or acetone. Uranium compounds are dissolved in numerous solvents and solvent combinations such as water, mineral acids, organic solvents such as acetone, alcohols, and diethyl ether. Dissolution of uranium from minerals and ores is accomplished by decomposition of the sample or leaching the uranium. Grinding and roasting the sample facilitates recovery. Decomposition of the sample can be accomplished with mineral acids or by fusion or a combination of the two processes. Hydrofluoric acid aids the process. The sample can be fused with sodium carbonate, sodium hydroxide, sodium peroxide, sodium bisulfate, ammonium sulfate, lithium metaborate, and magnesium oxide. The fused sample is dissolved in water or acid. Acid and alkaline mixtures are used to leach uranium from minerals and ores. The procedures employ common mineral acids or alkaline carbonates, hydroxides, and peroxides. Liquid biological samples may also be extracted to remove uranium, or the solid sample can be ashed by a wet or dry process and dissolved in acid solution. Wet ashing is carried out with nitric acid and completed with perchloric acid, but extreme caution should be used when using perchloric acid in the presence of organic material. Such mixtures have been known to detonate if the perchloric acid is allowed to dry out.

Separation Methods

PRECIPITATION AND COPRECIPITATION. There are a large number of reagents that will precipitate uranium over a wide pH range. The number of reagents available coupled with the two possible oxidation states of uranium in solution and the complexing properties of the ions provide many opportunities to separate uranium from other cations and the two oxidation states from each other. Precipitation can be inhibited, for example, by the presence of complexing agents that form soluble complexes. Complexes that form weak complexes with uranium and strong complexes with other cations allow the separation of uranium by its precipitation while the complexed cations remain in solution. EDTA has been used in this manner to separate uranium from many of the transition metals and alkaline earths. In contrast, uranium forms a very strong soluble complex with carbonate, and this property has been used to keep uranium in solution while ammonium hydroxide precipitates iron, titanium, zirconium, and aluminum. In a similar manner, uranium is separated from other cations as they are precipitated as sulfides or phosphates. Common precipitating reagents include:

- Ammonium hydroxide, which precipitates uranium quantitatively at pH ≥ 4;
- Carbonate [however, it will form soluble anionic complexes with U(VI) at pH 5 to 11 while many other metals form insoluble hydroxides];
- Peroxide;
- Oxalic acid, which completely precipitates uranium (+4) while U(VI) forms a soluble complex;
- Iodide;
- Iodate;
- Phosphate for U(VI) over a wide pH range;

- Sulfate;
- Cupferron, which precipitates uranium (+4) from an acidic solution but U(VI) from a neutral solution; and
- 8-hydroxyquinoline, which forms a quantitatively precipitate with U(VI) only.

Coprecipitation of uranium is accomplished with several carriers. In the absence of carbonate, it is quantitatively coprecipitated with ferric hydroxide at pH from 5 to 8. Aluminum and calcium hydroxide are also employed to coprecipitate uranium. Uranium(VI), however, is only partially carried by metal hydroxides in the presence of carbonate, and the amount carried decreases as the concentration of carbonate increases. Small amounts of U(VI) coprecipatate with ceric and thorium fluoride, calcium, zirconium, and aluminum phosphate, barium carbonate, thorium hexametaphosphate, magnesium oxide, and thorium peroxide. Uranium (+4) is carried on ceric sulfate, the phosphates of zirconium, bismuth, and thorium, lanthanum and neodymium fluoride, ceric and zirconium iodates, barium sulfate, zirconium phosphate, and bismuth arsenate.

SOLVENT EXTRACTION. Liquid-liquid extraction is the most common method for the separation of uranium in radioanalytical procedures. Extraction provides a high-recovery, one-batch process that is more reproducible than other methods. With the development of extraction chromatography, solvent extraction has become a very efficient process for uranium separation. Many and varied procedures are used to extract uranium from aqueous solutions, but the conditions can be summarized as: (1) composition of the aqueous phase (form of uranium, type of acid present, and presence of common cations and anions and of foreign anions); (2) nature of organic phase (type and concentration of solvent and diluent); (3) temperature; and (4) time of equilibrium. Extraction processes can be conveniently divided into three systems: those based on (1) oxygen bonding, (2) chelate formation, and (3) extraction of anionic complexes.

Oxygen-bonding systems are more specific than those based on chelate formation. They employ organic acids, ethers, ketones, esters, alcohols, organophosphates (phosphoesters), and nitroalkanes. Ethers are effective for the extraction of uranyl nitrate from nitric acid solutions. Cyclic ethers are especially effective, and salting agents such as calcium nitrate increase the effectiveness. Methyl isobutyl ketone (MIBK or hexone) also effectively extracts uranium as the nitrate complex. It has been used extensively by industry in the Redox process for extracting uranium and plutonium from nuclear fuels. Aluminum hydroxy nitrate [$AlOH(NO_3)_2$] is an excellent salting agent for the process and the extraction efficiency is increased by the presence of the tetrapropylammonium cation [$(C_3H_7)_4N^{+1}$]. Another common system, used extensively in the laboratory and in industrial process to extract uranium and plutonium from fission products, known as the PUREX process, is used in most fuel reprocessing plants to separate the radionuclides. It employs TBP, tri-*n*-butyl phosphate [$(C_4H_9)_3PO$], in a hydrocarbon solvent, commonly xylene/toluene, as the extractant. The uranium fuel is dissolved in nitric acid, and uranium and plutonium are extracted into a 30 percent TBP solution, forming a neutral complex, $UO_2(TBP)_2$. The organic phase is scrubbed with nitric acid solution to remove impurities, plutonium is removed by back-extracting it as Pu^{+3} with a nitric acid solution containing a reducing agent, and uranium is removed with dilute nitric acid. A complexing agent can also be used as a stripping agent. Trioctylphosphine oxide is 100,000 times more efficient in extracting U(VI). In both cases, nitric acid is used both to form the uranium extracting species, uranyl nitrate, and as the salting agent. Salting with aluminum nitrate produces a higher extraction efficiency but less specificity for uranium. Specificity depends upon the salt used, its concentration, and the diluent concentration.

Uranium is also extracted with select chelate forming agents. One of the most common systems used for uranium is cupferron in diethyl ether or chloroform. Uranium(VI) is not extracted from acidic media, so impurities soluble in the mixture under acidic conditions can be extracted first. Uranium(VI) can be reduced to U^{+4} for subsequent extraction. Other chelating agents used to extract uranium include 8-hydroxyquinoline, acetylacetone in hexone, or chloroform.

Amines with molecular weights in the 250 to 500 range are used to extract anionic complexes of U(VI) from acidic solutions. The amine forms a salt in the acidic medium consisting of an ammonium cation and complex anion, $(C_{10}H_{21})_3NH^{+1}\ UO_2(NO_3)^{-1}$, for example. Selectivity of the amines for U(VI) is in the order: tertiary > secondary > primary. An anionic extracting system used extensively in laboratories and industry consists of triisooctyl amine (TIOA) in xylene/toluene. Uranium is stripped with sodium sulfate or sodium carbonate solution. A number of mineral and organic acids have been used with the system: hydrochloric, sulfuric, nitric, phosphoric, hydrofluoric, acetic oxalic, formic, and maleic acid. Stripping is accomplished with dilute acid solutions.

Extraction chromatography is a simple and relatively quick method for the separation of uranium on a highly selective, efficient column system. One separation column consists of a triamylphosphate $[(C_5H_{11}O)_3PO]$ and diamylamylphosphonate (DAAP) $[C_5H_{11}O)_2(C_5H_{11})PO]$ mixture in an apolar polymeric matrix. In nitric acid, uranyl nitrate forms a complex with DAAP that is soluble in triamylphosphate. Uranium can be separated in this system from many other metal ions including thorium and the transuranium ions, plutonium, americium, and neptunium. It is eluted from the column with the addition of oxalate to the eluent. Another extraction chromatography column uses CMPO dissolved in TBP and fixed on the resin matrix for isolation of uranium in nitric acid. Elution occurs with the addition of oxalic acid to the eluent.

ION-EXCHANGE CHROMATOGRAPHY. Both cation- and anion-exchange chromatography have been used to separate uranium from other metal ions. Both stable forms of uranium, uranium +4 and VI are exchanged onto cation-exchange resins. Uranium (+4) is more strongly exchanged, and separation of U(VI) (UO_2^{+2}) is limited. On some cation-exchange columns, the ion also tends to tail into other ion fractions during elution. Exchange increases with temperature, however, and increasing the pH also increases exchange up to the beginning of formation of hydrolytic precipitates at pH 3.8. In strong acid solutions, U(VI) is weakly absorbed compared to uranium (+3 and +4) cations. Using complexing agents can increase specificity by elution of U(VI) with common complex-forming anions, such as chloride, fluoride, nitrate, carbonate, and sulfate.

Specificity also may be enhanced by forming EDTA, oxalate, acetate, or sulfate complexes with cations in the analyte, producing a more pronounced difference in absorption of the ions on the exchange resin. A general procedure for separating U(VI) from other metals using the first method is to absorb U(VI) at pH of 1.5 to 2 and elute the metal with acetate solution.

Anion-exchange chromatography of uranium takes advantage of the stable anionic complexes formed by the various oxidation states of uranium, especially U(VI), with many common anions. Uranium(VI) forms both anionic or neutral complexes with acetate, chloride, fluoride, carbonate, nitrate, sulfate, and phosphate. Strong anion-exchange resins are more selective and have a greater capacity than weak exchangers whose use is more limited. Factors that affect the separations include uranium oxidation state and concentration; type of anion and concentration; presence and concentration of other metallic ions and foreign ions; temperature, resin, size, porosity, and cross-linking. The various oxidation states of uranium and other metal ions (particularly the actinides), the effect of pH on formation of complexes, and the net charge of the column are all variables controlling the separation process.

A number of chromatographic systems are available for uranium separation on anion-exchange resins. In hydrochloric acid, uranium is often exchanged and other cations are not. Uranium(VI) can be exchanged from concentrated hydrochloric acid while alkali metals, alkaline earths, rare earths, aluminum, yttrium, actinium, and thorium are washed off the column. In contrast, uranium, molybdenum, bismuth, tin, technetium, polonium, plutonium and many transition metals are exchanged on the column, and uranium is eluted exclusively with dilute hydrochloric acid. Various oxidation states provide another method of separation. U^{+4} is separated from Pr^{+4} and Th^{+4} with 8 M hydrochloric acid. Thorium, plutonium, zirconium, neptunium, and uranium can be separated individually by exchanging all the ions except thorium from concentrated hydrochloric acid. Plutonium (+3) elutes with concentrated acid, zirconium at 7.5 M, Np^{+4} with 6 M hydrochloric acid and 5 percent hydroxylamine hydrochloride, and uranium at 0.1 M acid. U^{+4} can be separated from U(VI) because both strongly exchangefrom concentrated hydrochloric acid, but they separate at 6 M acid because U^{+4} is not exchanged at that concentration. Uranium(VI) exchanges strongly on an anion-exchange resin in dilute hydrofluoric acid, and the exchange decreases with increasing acid concentration. Nitric acid provides an excellent method to purify uranium, because uranium is more strongly exchanged from nitric acid/nitrate solutions than from chloride/HCl solutions. More selectivity is achieved when acid concentration is low and nitrate concentrations are high. Exchange is greatest when aluminum nitrate is use as the source of nitrate. Ethyl alcohol increases exchange significantly.

ELECTRODEPOSITION. Electrochemical procedures have been used to separate metal ions from uranium in solution by depositing them on a mercury cathode from a sulfuric acid solution, using 5 amps for one hour. Uranium is deposited at a cathode from acetate, carbonate, oxalate, formate, phosphate, fluoride, and chloride solutions to produce a thin, uniform film for alpha and fission counting. This is the primary use of electrodeposition of uranium in analytical work. In another procedure, U(VI) is electroplated on a platinum electrode from the basic solution adjacent to the cathode that exists in a slightly acidic bulk solution. The conditions of the process should be carefully controlled to obtain high yields and adherent coatings on the electrode.

VOLATILIZATION. Several halides of uranium and the uranyl ion are volatile and have the potential for separation by sublimation or fractional distillation. Practically, however, their volatility is not used to separate uranium in analytical procedures because of technical problems or the high temperatures that are required for some procedures, but volatilization has been used in industrial processes. Uranium hexafluoride and uranyl hexafluoride are volatile, and the property is used to separate ^{235}U from ^{238}U in natural uranium isotope mixtures. Uranium tetrachloride and hexachloride are also volatile, and uranium has been isolated from phosphate rock by heating with a mixture of chlorine and carbon monoxide at 800 °C and collecting the tetrachloride.

Methods of Analysis

Uranium may be determined by fluorimetry. During the separation and purification process, the sample is fused at 625 °C in a flux mixture containing potassium carbonate, sodium carbonate, and sodium fluoride. The residue is exposed to light and its fluorescence is measured. Another technique related to fluorescence is kinetic phosphorimetry analysis (KPA). Aqueous solutions of the fully digested sample are exposed to a laser at a specific wavelength, and the phosphorescence (at a different wavelength) intensity is measured.

Total uranium may be determined by gross alpha analysis. Individual radionuclides of uranium, ^{234}U, ^{235}U, and ^{238}U, can be determined by their alpha-particle emissions. Mass spectrometry also can be used for longer-lived isotopes of uranium. Uranium radionuclides are collected by evaporating the sample to dryness on a stainless steel planchet, by microprecipitation with a carrier, such as lanthanum or cerium fluoride, or electrodeposition on a platinum or stainless-steel disc. In each of these techniques, care must be taken to ensure that a single oxidation state is achieved for the uranium prior to the collection technique. Total alpha activity is determined with a gas-flow proportional counter or an alpha liquid scintillation system. Individual radionuclides are measured by alpha spectrometry. Alpha emissions from ^{232}U are used as a tracer to determine chemical recovery.

Neutron activation analysis (NAA) was employed to determine uranium in the hydrogeochemical samples from Savannah River Plants within the scope of the National Uranium Resource Evaluation Program sponsored by DOE. Uranium was determined by cyclic activation and delayed neutron counting of the ^{235}U fission products. The method relied on absolute activation techniques using the Savannah River Reactor Activation Facility. NAA, followed by delayed-neutron detection, was commonly used to determine ^{235}U.

Compiled from: Alfassi, 1990; Allard et al., 1984; Ahrland, 1986; Baes and Mesmer, 1976; ASTM D5174; Bard, 1985; Booman and Rein, 1962; Choppin et al., 1995; Considine and

Considine, 1983; Cotton and Wilkinson, 1988; CRC, 1998-99; DOE, 1990 and 1997; Echo and Turk, 1957; EPA, 1973; Ehmann and Vance, 1991; Fritz and Weigel, 1995; Greenwood and Earnshaw, 1984; Grindler, 1962; Hampel, 1968; Hassinsky and Adloff, 1965; Hochel, 1979; Katz et al., 1986; Katzin, 1986; SCA, 2001; Weigel, 1986.

14.10.9.16 Zirconium

Zirconium, atomic number 40, is a member of the second-row transition elements. It exhibits oxidation states of +2, +3, and +4, and the +4 state is common in both the solid state and in solution. It is immediately above hafnium in the periodic table, and both elements have very similar chemical properties—more so than any other two elements in the periodic table. It is very difficult, but not impossible, to prepare a sample of zirconium without the presence of hafnium.

Isotopes

There are twenty-nine isotopes of zirconium, including five metastable states, with mass numbers from 81 through 104. Five are naturally occurring, ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr, and ^{96}Zr. The remaining isotopes have a half-life of milliseconds to days. The lower mass number isotopes decay primarily by electron capture and the upper mass number isotopes are beta emitters. Zirconium-95 ($t_{1/2} \approx 64.0$ d) and ^{97}Zr ($t_{1/2} \approx 16.9$ h) are fission products and are beta emitters. Zirconium-93 ($t_{1/2} \approx 1.53\times10^6$y) is a rare fission product, and ^{98}Zr, and ^{99}Zr are short-lived products with half-lives of 30.7 s and 2.1 s, respectively. All are beta emitters.

Occurrence and Uses

Zirconium is one of the most abundant and widely distributed metals found in the Earth's crust. It is so reactive that it is found only in the combined state, principally in two minerals, zircon, zircon orthosilicate ($ZrSiO_4$), and baddeleyite, mostly zirconium dioxide (ZrO_2). Zirkite is a commercial ore that consists of both minerals. Hafnium is a minor constituent of all zirconium minerals.

In the production of zirconium metal, zirconium sands, primarily zirconium dioxide, is passed through an electrostatic separator to remove titanium minerals, a magnetic separator to remove iron, ileminite, and garnet, and a gravity separator to remove the less dense silica. The recovered zircon is heated with carbon in an arc furnace to form zirconium cyanonitride, an interstitial solution of carbon, nitrogen, and oxygen (mostly carbon) in the metal. Silicon evaporates as silicon monoxide (SiO), becoming silicon dioxide (SiO_2) at the mouth of the furnace. The hot zirconium cyanonitride is treated with chlorine forming volatile zirconium tetrachloride ($ZrCl_4$), which is purified by sublimation to remove, among other impurities, contaminating oxides. The chloride is reduced in the Kroll process, along with liquid magnesium under conditions that produce a metal sponge. The byproduct, magnesium chloride ($MgCl_2$), is then removed by melting the chloride, draining it off, and removing its residues by vacuum distillation. The zirconium sponge is crushed, melted into bars, arc-melted in an inert atmosphere, and formed into ingots. For additional purification, the van Arkel-de Boer process removes all nitrogen and oxygen. Crude zirconium is heated to 200 °C in an evacuated container containing a small amount of iodine to form volatile zirconium tetraiodide (ZrI_4). A tungsten filament is electrically heated to 1,300 °C, decomposing the iodide and depositing zirconium on the filament. The commercial grade of zirconium still contains up to three percent hafnium. To be used in nuclear reactors, however, hafnium should be removed. Separation is usually accomplished by solvent extraction of zirconium from an aqueous solution of zirconium tetrachloride as a complex ion (phosphine oxide, for example), by ion-exchange, fractional crystallization of complex fluoride salts, distillation of complexes of zirconium tetrachloride with phosphorus pentachloride or phosphorus oxychloride, or differential reduction of the mixed tetrachlorides (zirconium tetrachloride is more easily reduced to the nonvolatile trichloride than hafnium tetrachloride.

Zirconium-95 and ^{97}Zr are fission products and are also produced by bombardment of naturally occurring ^{94}Zr and ^{96}Zr, respectively, with thermal neutrons. Stable ^{90}Zr is a product of the ^{90}Sr decay chain:

$$^{90}_{38}\mathrm{Sr} \rightarrow {}^{90}_{39}\mathrm{Y} + \beta \rightarrow {}^{90}_{40}\mathrm{Zr} + \beta$$

Zirconium metal and its alloys are highly resistant to corrosion and withstand streams of heated water under high pressure. These properties, along with their low cross section for thermal neutrons, make them an important material for cladding uranium fuel elements and as core armor material in nuclear reactors. It is also used for making corrosive resistant chemical equipment and surgical instruments and making superconducting magnets. Zirconium compounds are also used in the ceramics industry as refractories, glazes, and enamels, in cores for foundry molds, abrasive grits, and components of electrical ceramics. Crystals of zircon are cut and polished to use in jewelry as simulated diamonds. They are also used in pyrotechnics, lamp filaments, in arc lamps, cross-linking agents for polymers, components of catalysts, as bonding agents between metal and ceramics and between ceramics and ceramics, as tanning agents, ion exchangers, and in pharmaceutical agents as deodorants and antidotes for poison ivy. Zirconium-95 is used to follow homogenization of oil products.

Solubility of Compounds

The solution properties of zirconium in water are very complex, mainly because of the formation of colloids and the extensive hydrolysis and polymerization of the zirconium ion. hydrolysis and polymerization are strongly dependent on the pH of the solution, concentration of the ion, and temperature. The nitrate, chloride, bromide, iodide, perchlorate, and sulfate of zirconium are soluble in acid solution, however.

Review of Properties

Pure zirconium is a grey-white (silvery) lustrous metal with a density of 6.49 g/cm^3. It exists in two allotropic forms, alpha and beta, with a transition temperature of 870 °C. The alpha form is stabilized by the common impurity oxygen. The amorphous powder is blue-black. Trace amounts of common impurities (≤ 1 percent), such as oxygen, nitrogen, and carbon, make the metal brittle and difficult to fabricate. The metal is not considered to be a good conductor of heat and electricity, but compared to other metals it is soft, malleable, and ductile. Zirconium forms alloys with most metals except mercury, the alkali metals, and the alkaline earths. It can absorb up to ten percent oxygen and nitrogen. Zirconium is a superconductor at temperatures near absolute zero, but its superconducting properties improve when the metal is alloyed with niobium and zinc.

Finely divided, dry zirconium (powder and chips) is pyrophoric and extremely hazardous. It is hard to handle and store and should be moistened for safe use. Note, however, that both wetted sponge and wet and dry stored scrap have been reported to spontaneously explode. Caution should also be observed with waste chips produced from machining and cleaning (new) zirconium surfaces. Both can be pyrophoric. In contrast, zirconium in the bulk form is extremely resistant to corrosion at room temperature and remains bright and shiny in air. Resistance is rendered by the formation of a dense, adherent, self-sealing oxide coating. The metal in this form is resistant to acids, alkalis, and seawater. Without the coating, zirconium dissolves in warm hydrochloric and sulfuric acids slowly; dissolution is more rapid in the presence of fluoride ions. The metal is also resistant to high-pressure water streams and high-temperature steam. It also has a low cross-section to thermal neutrons and is resistant to damage from neutron radiation. These properties give pure zirconium (without hafnium) very useful as a fabrication material for nuclear reactors. Zirconium metal alone, however, is not sufficiently resistant to hot water and steam to meet the needs for use in a nuclear reactor. Alloyed with small percentages of tin, iron, nickel, or chromium (Zircalloy), however, the metal meets the standards.

The coated metal becomes reactive when heated at high temperature ($\geq$ 500 °C) with nonmetals, including hydrogen, oxygen, nitrogen, carbon, and the halogens, and forms solid solutions or compounds with many metals. It reacts slowly with hot concentrated sulfuric and hydrochloric acids, boiling phosphoric acid, and aqua regia. It is also attacked by fused potassium nitrate and potassium hydroxide, but is nonreactive with aqueous alkali solutions. It is not reactive with nitric acid. Hydrofluoric acid is the only reagent that reacts vigorously with zirconium.

Zirconium and its compounds are considered to have a low order of toxicity. Most handling and testing indicate no level of toxicity, but some individuals seem to be allergic to zirconium compounds. Inhalation of zirconium compound sprays and metallic zirconium dust have produced inflammatory affects.

Very small quantities of ^{95}Zr have been released to the environment from fuel reprocessing facilities, atmospheric testing, and the Chernobyl accident. With a half-life of 64 days, the contamination of the environment is not significant. Zirconium lost from a waste repository would be expected to move very slowly because of radiocolloidal attraction to surrounding soil particles. Hydrolysis and polymerization renders most zirconium insoluble in natural water, but absorption to suspended particles is expected to provide some mobility in an aqueous environment.

Solution Chemistry

The only important oxidation state of zirconium ions in aqueous solution is +4. The solution chemistry of zirconium is quite complex, nevertheless, because of the easy formation of colloids and extensive hydrolysis and polymerization reactions that are strongly dependent on pH and ion concentration.

COMPLEXATION. Zirconium ions form complexes with numerous substances: fluoride, carbonate, borate, oxalate, and other dicarboxylic acids, among others. As a large, highly charged, spherical ion, it exhibits high coordination numbers. One of the important chemical properties of zirconium ions in solution is the formation of a very stable hexafluorozirconate complex, ZrF_6^{-2}. For that reason, hydrofluoric acid (HF) is an excellent solvent for the metal and insoluble zirconium compounds. Unfortunately, the fluorocomplex interferes with most separation and determination steps, and zirconium should be expelled by fuming with sulfuric or perchloric acid before proceeding with analyses of other radionuclides. The addition of several milliliters of concentrated HF to a cool solution of zirconium carrier and sample will produce initial equilibration; essentially all the zirconium is present in the +4 oxidation state as a fluoride complex. Note that addition of HF to solutions above the azeotropic boiling point of the acid (120 °C) serves no useful purpose and simply evaporates the HF.

Tartrate and citrate ions form stable complexes even in alkaline solutions, and zirconium hydroxide will not precipitate in their presence (see hydrolysis below). Oxalate forms a complex that is less stable. The ion, $[Zr(C_2O_4)_3]^{-2}$, is only stable in acid solution. On addition of base, the complex is destroyed, and zirconium hydroxide precipitates. Sulfuric acid complexes in strongly acidic solutions, forming $Zr(SO_4)_3^{-2}$. In concentrated HCl solutions, $ZrCl_6^{-2}$ is present.

Zirconium ions form chelate complexes with many organic compounds, usually through oxygen atoms in the compounds. Typical examples are: acetylacetone (acac), EDTA, TTA, salicylic acid, mandelic acid, cupferron, and 8-hydroxyquinoline.

HYDROLYSIS. Although Zr^{+4} has a large radius and any +4 cation is extensively hydrolyzed, Zr^{+4} appears to exist at low ion concentrations (approximately 10^{-4} M) and high pH. As the Zr^{+4} concentration increases and the concentration of H^{+1} decreases, however, hydrolysis and polymerization occurs, and one or more polymeric species dominates in solution. Amorphous hydrous oxides are precipitated near pH 2; they are soluble at high pH. Because of hydrolysis, soluble salts (nitrate, sulfate, perchlorate, acetate, and halides) form acidic solutions when they dissolve. The reaction essentially seems to be a direct conversion to the tetranuclear $Zr_4(OH)_8(H_2O)_{16}^{+8}$ ion. There is no convincing evidence for the existence of ZrO^{+2}, thought at one time to be present in equilibrium with numerous other hydrolysis products. It should be noted, however, that freshly prepared solutions of zirconium salts might react differently from a solution left standing for several days. Whatever the actual species in solution at any given time, the behavior of Zr^{+4} depends on the pH of the solution, temperature, anion present, and age of solution. In addition, zirconium compounds formed by precipitation from solution usually do not have a constant composition because of their ease of hydrolysis. Even under exacting conditions, it is difficult to obtain zirconium compounds of known, theoretical composition, and on aging, hydrolysis products becomes more polymeric and polydisperse.

In acidic solutions, trace amounts of zirconium are strongly coprecipitated with most precipitates in the absence of complexing ions, especially F^{-1} and $C_2O_4^{-2}$ that form soluble complex ions.

In alkaline solutions, produced by the addition of hydroxide ions or ammonia, a white gelatinous precipitate of zirconium hydroxide forms. Because the hydroxide is not amphoteric, it does not dissolve in excess base. The precipitate is not a true hydroxide but a hydrated oxide, $ZrO_2 \cdot nH_2O$ where *n* represents the variable nature of the water content. Freshly prepared zirconium hydroxide is soluble in acid; but as it dries, its solubility decreases. Precipitation is inhibited by tartrate or citrate ions because Zr^{+4} forms complexes with these organic anions even in alkaline solutions (see "Complexation," on page 14-194, above).

In preparing zirconium solutions, it is wise to acidify the solution with the corresponding acid to reduce hydrolysis and avoid precipitation of basic salts. During solubilization and radiochemical equilibrium with a carrier, the tendency of zirconium ions to hydrolyze and polymerize even at low pH should be kept in mind. Often, the formation of a strong complex with fluoride or TTA is necessary.

RADIOCOLLOIDS. Radiocolloids of zirconium are adsorbed on practically any foreign matter (e.g., dirt, glass, etc.). Their formation can cause problems with dissolution, achieving radiochemical equilibrium, and analysis. Generally, it is necessary to form a strong complex with fluoride (see caution above) or TTA.

Dissolution of Samples

Metallic zirconium is dissolved in hydrofluoric acid, hot aqua regia, or hot concentrated sulfuric acid. Hydrofluoric acid should be removed by fuming with sulfuric acid or perchloric acid (caution), because fluoride interferes with most separation and analytical procedures. Zirconium ores, rocks, and minerals are fused at high temperatures with sodium carbonate, potassium thiosulfate, sodium peroxide, sodium tetraborate, or potassium hydrogen fluoride. The residue is dissolved in dilute acid or water and might require filtration to collect a residue of zirconia (impure ZrO_2), which is dissolved in acid. As a minor constituent of natural sample or as a result of formation by nuclear reactions, zirconium typically dissolves during dissolution of the major constituents. The tendency to polymerize under low concentrations of acid and the formation of insoluble zirconium phosphates should be considered in any dissolution process. The tendency of zirconium to polymerize and form radiocolloids makes it important to insure equilibrium with any carrier added. Generally, formation of strong complexes with fluoride or TTA is necessary.

Separation Methods

PRECIPITATION AND COPRECIPITATION. One of the most insoluble precipitating agents is ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) in 20 percent sulfuric acid. It has the advantage that it can be dissolved by hydrofluoric acid, forming hexafluorozirconate. This complex ion also forms insoluble barium hexafluorozirconate ($BaZrF_6$), a precipitating agent that allows the precipitation of zirconium in the presence of niobium that is soluble as the heptafluoroniobate (NbF_7^{-2}). Other precipitating agents include the iodate (from 8 M nitric acid), cupferrate, the hydroxide, peroxide, selenate, and mandelate. Cupferron is used in sulfuric or hydrochloric acid solutions. It is one of the few precipitating agents in which fluoride does not interfere, but iron and titanium, among other cations, are also precipitated. The precipitate can be heated in a furnace at 800 °C to produce zirconium dioxide for the gravimetric determination of zirconium. The hydroxide begins to precipitate at pH 2 and is complete at pH 4, depending on the presence of zirconium complexes. It is not recommended unless other cations are absent, because it absorbs or coprecipitates almost all other ions. Peroxide is formed from a solution of hydrogen peroxide in acid. Selenious acid in dilute hydrochloric acid separates zirconium from some of the transition elements and thorium. Mandelic acid in hot dilute hydrochloric acid quantitatively and specifically precipitates zirconium (and hafnium) ions. Large amounts of titanium, tin, iron, and other ions might be partially coprecipitated, but they can be eliminated by reprecipitation.

Trace quantities of zirconium can be strongly coprecipitated by most precipitates from strong acid solutions that do not contain complex-forming ions. Bismuth and ceric phosphate readily carries zirconium, and in the absence of holdback carriers, it is almost quantitatively carried by rare-earth fluorides. Ferric hydroxide and thorium iodate are also effective carriers.

SOLVENT EXTRACTION. Several extractants have been used to selectively remove zirconium from aqueous solutions; most are organophosphorus compounds. Di-*n*-butylphosphoric acid (DBPA) (di-*n*-butylphosphate) is an extractant for zirconium and niobium. It is effective in extracting tracer and macro quantities of zirconium from 1 M aqueous solutions of nitric, hydrochloric, perchloric, and sulfuric acids and in separating it from many other elements. A 0.06 M solution in di-*n*-butylether containing three percent hydrogen peroxide extracts more than 95 percent zirconium but less than one percent niobium. Tin and indium were also extracted by this mixture. TBP is an excellent solvent for zirconium. It is used pure or with several nonpolar diluents, such as ethers, xylene/toluene, or carbon tetrachloride. Extractability increases with acid strength. A 0.01 M solution of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane has been used to separate zirconium from iron, molybdenum, vanadium, thorium, and hafnium.

TTA and hexone (methyl isobutyl ketone) are two nonphosphorus extractants employed for separating zirconium. TTA is highly selective. A 0.5 M solution in xylene separates zirconium from aluminum, iron, thorium, uranium, and rare earths in a 6 M hydrochloric acid solution. At tracer levels, the reagent can separate ^{95}Zr from all other fission products. It is also used to separate zirconium from hafnium. In the analysis of zirconium in zirconium-niobium-tantalum alloys, hexone separates zirconium from an aqueous solution that is 10 M hydrochloric acid and 6 M sulfuric acid. This is one of the few methods that can be used to separate zirconium from such metals.

ION-EXCHANGE CHROMATOGRAPHY. Zirconium can be separated from many other cations by both cation- and anion-exchange chromatography. The technique represents the best laboratory method for separating zirconium and hafnium. Cation-exchange columns strongly exchange zirconium ions, but macro quantities of zirconium and hafnium can be purified as aqueous colloidal solutions of their hydrous oxides on an organic cation-exchange resin. Many cations are retained on the column, but zirconium and hafnium, under these conditions, are not. The recovery can be as high as 99 percent with successive passages, but titanium and iron are not removed. Zirconium and hafnium can be separated on a sulfuric-acid column from 2 M perchloric acid. Hafnium is eluted first with 6 M HCl. Fluoride complexes of zirconium and hafnium can be separated from other noncomplexing cations, because the negative complex ions are not exchanged, and the noncomplexing ions are retained. Zirconium, hafnium, and niobium are eluted from rare earths and alkaline earths on cation-exchange columns with citrate. The three elements can be then be separated by the selection of appropriate citrate buffers, but the separations are not quantitative.

The formation of stable zirconium complexes is the basis of anion-exchange chromatography of the metal. Separation of zirconium and hafnium from each other and from other cations can be achieved in hydrochloric-hydrofluoric acid mixtures. Separation of zirconium from hafnium, niobium, protactinium, and thorium, respectively, is accomplished by selection of the proper eluting agent. Elution of hafnium first with 9 M hydrochloric acid separates zirconium from hafnium, for example, while elution with 0.2 M hydrochloric acid/0.01M hydrofluoric acid recovers zirconium first. Elution with 6-7 M hydrochloric acid separates zirconium from niobium, in another example.

Methods of Analysis

Zirconium-95 decays with a half-life of 65.5 d, emitting a beta particle accompanied by gamma-ray emission. After several half-lives, it is in transient equilibrium with its progeny, ^{95}Nb, which has a half-life of 35.0 d and is also a beta and gamma emitter. The progeny of ^{95}Nb is stable ^{95}Mo. Fresh samples of ^{95}Zr are analyzed by their gamma-ray emission. Zirconium is collected by precipitation and filtration. The sample and filter are heated at 800 °C for one hour to decompose the filter and convert zirconium to its oxide. Zirconium dioxide (ZrO_2) is collected by filtration, dried, and counted immediately.

Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Considine and Considine, 1983; Cotton and Wilkinson, 1988; CRC, 1998-99; Ehmann and Vance, 1991; EPA, 1973; Greenwood and Earnshaw, 1984; Hahn, 1961; Hassinsky and Adloff, 1965; Latimer, 1952; Steinberg, 1960.

14.10.9.17 Progeny of Uranium and Thorium

The analysis of uranium and thorium isotopes is most frequently performed by alpha spectroscopic, liquid scintillation, mass spectrometry, or proportional-counting analysis. The analyst frequently is focused on the uranium and thorium analytes and can readily forget that the progeny of these isotopes also are radioactive. In fact, the decay chains may contain 10 to 14 different isotopes that all decay by beta or alpha emission. The radioactive progeny are analytes of importance in their own right. Thus, the analytical focus could be on the parent isotopes or on any of these progeny. It is important not to lose sight of the fact that even after separations the radioactive decay process continues, and new progeny are formed.

The elements that interfere most (due to their activities) with analysis of transuranics are radium, radon, actinium, lead, bismuth, and polonium. Radium, radon, and actinium form a group based on the decay of their isotopes and the relative half-lives of those isotopes. Lead, polonium, and bismuth form a "group," which are discussed separately as "contaminants" in the analysis of the transuranics or radium. There are specific analytical schemes for each of these that are developed in separate references.

Radium and Radon

Naturally occurring uranium and thorium give rise to the following principal radioisotopes of radium and radon:

$$^{238}\text{U} \xrightarrow{\alpha} {}^{234}\text{Th} \xrightarrow{\beta} {}^{234}\text{Pa} \xrightarrow{\beta} {}^{234}\text{U} \xrightarrow{\alpha} {}^{230}\text{Th} \xrightarrow{\alpha} {}^{226}\text{Ra} \xrightarrow{\alpha} {}^{222}\text{Rn} \qquad [\text{U-1}]$$

$$^{232}\text{Th} \xrightarrow{\alpha} {}^{228}\text{Ra} \xrightarrow{\beta} {}^{228}\text{Ac} \xrightarrow{\beta} {}^{228}\text{Th} \xrightarrow{\alpha} {}^{224}\text{Ra} \xrightarrow{\alpha} {}^{220}\text{Rn} \qquad [\text{Th-1}]$$

The presence of these isotopes in natural waters, soils, and buildings poses a level of radiological risk from exposure to gross alpha and beta emitters, which can result from diffusion of the radon gas or radium solubility. The primordial radium and radon atoms have long since decayed, so both elements now result from the decay of uranium and thorium.

If these decay chains were unaffected by the environment, secular equilibrium (Attachment 14A, "Radioactive Decay and Equilibrium") of uranium, thorium, and all their respective progeny would have occurred millions of years ago. This would mean that the analysis of the whole decay chain could be performed by measuring one radionuclide's activity and using the Bateman equations to calculate the other activities. However, the noble gas chemistry of radon and the differential solubility of the other isotopes cause these chains to be disrupted or "broken." The latter part of the decay chain contains the isotopes of polonium, bismuth, and lead and are sometimes separately identified due to the break in the chain at radon.

Radon is an indoor exposure hazard because it can seep through barriers, such as concrete foundations. It will form its own radiochemical chain from its decay as parent to isotopes of the polonium/bismuth/lead group:

$$^{222}\text{Rn} \xrightarrow{\alpha} {}^{218}\text{Po} \xrightarrow{\alpha} {}^{214}\text{Pb} \xrightarrow{\beta} {}^{214}\text{Bi} \xrightarrow{\beta} {}^{214}\text{Po} \xrightarrow{\alpha} {}^{210}\text{Pb} \xrightarrow{\beta} {}^{210}\text{B} \xrightarrow{\beta} {}^{210}\text{Po} \xrightarrow{\alpha} {}^{206}\text{Pb} \qquad \text{[Rn-1]}$$

$$^{220}\text{Rn} \xrightarrow{\alpha} {}^{216}\text{Po} \xrightarrow{\alpha} {}^{212}\text{Pb} \xrightarrow{\beta} {}^{212}\text{Bi} \xrightarrow{\beta} {}^{212}\text{Po} \xrightarrow{\alpha} {}^{208}\text{Pb} \qquad \text{[Rn-2]}$$

The inert characteristic of the radon allows it to transport radioactivity to locations distant from the source. With chemical characteristics similar to calcium, however, radium will be similarly mobile in ground water. Thus, the analysis of radium and radon and their isotopes generally is done separately.

The chemistry of radium is detailed in Section 14.10.9.9. Direct analysis by the methods described will be satisfactory for large amounts of the material. The activity of radium found in many environmental or low activity samples represents an analytical challenge. The half-lives of the radium isotopes are quite long (^{228}Ra ≈ 5.8 y; ^{226}Ra ≈ 1,600 y). Thus, long counting times or very large samples are needed to achieve statistically relevant values at the minimum detectable level needed to meet regulatory requirements. Analytical methods have been developed to perform this task but suffer from large statistical error and from the handling of large samples. To circumvent these difficulties, indirect analytical techniques have been developed for each of these isotopes that rely on the chemistry of radium to obtain radiochemical purity, and on the Bateman equation of parent-progeny relationships to produce the shorter-lived progeny. The parent activity is determined by mathematical analysis from the progeny activity.

An example is in the analysis of ^{226}Ra. Radium is isolated by coprecipitation with barium as the sulfate. The precipitate is then dissolved according to the following:

$$\text{Ba/RaSO}_4 \xrightarrow{\text{EDTA}} \text{Ra/Ba(EDTA)}^{-2} \qquad \text{[Rn-3]}$$

The solution of radium complex is immediately transferred to a vessel (called a de-emanation tube) that is sealed under vacuum. This is a key aspect of the process, because the principal decay product is a noble gas. The decay of radium occurs according to [U-1] and [Th-1] above. According to the Bateman equations, after approximately 21 days, full equilibrium is established for [Rn-1]. Equilibrium for [Rn-2] is achieved in about 2 days. At the end of the equilibration period, the de-emanation tube is purged slowly with helium into a calibrated phosphorescence cell for counting. This removes the noble gas from all its progeny and parents, which are non-volatile. This time, however, equilibration is much shorter (on the order of four hours), and the analysis includes all of the progeny isotope emanations as well as those of the parents. The analysis for ^{222}Rn may have to be corrected for ^{220}Rn presence if thorium was a major contributor to the transuranic composition of the sample.

The remnant solution is used for the analysis of ^{228}Ra by exploiting the rapid achievement of secular equilibrium (already achieved) with its daughter isotope, ^{228}Ac, which is not volatilized during the nitrogen purge.

The radium isotopes again are removed by coprecipitation with barium as sulfates, but this time redissolved by diethylene triamine pentaacetic acid (DTPA).

$$(\mathrm{Ba/Ra})\mathrm{SO_4} \xrightarrow{\mathrm{DTPA}} [(\mathrm{Ba/Ra})(\mathrm{DTPA})]^{-3} \xrightarrow{20\%\ \mathrm{Na_2SO_4}} (\mathrm{Ba/Ra})\mathrm{SO4} \xrightarrow{\mathrm{DTPA}} [(\mathrm{Ba/Ra})(\mathrm{DTPA})]^{-3} \qquad [\mathrm{Rn\text{-}4}]$$

This is used to remove any residual ^{228}Ac. The solution of the DTPA complex is stored for a set period of time (usually about 36 hours), and the radium parent is removed by precipitation. The supernatant solution contains the actinium daughter. At the time of the separation, the actinium and radium activities are equal (see Attachment 14A, "Radioactive Decay and Equilibrium"). The activity of the actinium is determined and back-corrected to determine the radium activity.

Lead, Polonium, and Bismuth

Differential solubility and radon volatility play an important part of the spread of these naturally occurring radioisotopes in the environment. Looking at [Rn-1], the three most significant isotopes in this group are ^{210}Pb, ^{210}Bi, and ^{210}Po because of their half-lives. In [Rn-2], the significant isotope is ^{212}Pb, also because of its half-life. Both of these end-of-the-chain series can present problems in environmental analyses.

The purpose of the gross analysis is to be able to use a single, simple analysis as part of the decision process for requiring more complex analysis and dose estimation. The problem with gross alpha analysis, especially at the environmental level, is that it is subject to many sources of error. The most significant source of these errors has been shown to be the time between sample collection and analysis. In this case, elevated alpha activity was not attributed to $^{226/228}$Ra, but instead to ^{224}Ra. Radium-224, its short-lived decay-chain progeny including ^{212}Pb ($t_{1/2} \approx 10.6$ h), ^{212}Bi ($t_{1/2} \approx 1$ h), and ^{212}Po ($t_{1/2} << 1$ sec), were causing the variation in the activity. If the samples were counted too long after acquisition, gross alpha would be high due to the buildup of the short-lived progeny. Because the half-lives were measured in hours, a consistent time-after-sample needed to be established to standardize the buildup of the short-lived isotopes

Similarly, trying to account for the activity from alpha/beta emitters from the [Rn-1] chain is difficult because ^{210}Pb ($t_{½}$ ≈22.6 y) emits very low-energy beta particles and gamma rays and quickly reaches equilibrium with its bismuth and polonium progeny. An analysis for ^{210}Pb has been developed that is specific and sensitive. The lead present in the sample is chemically separated from the bismuth by precipitation. The bismuth is removed by washing, and only the bismuth produced by the lead decay is measured. This relies on the secular equilibrium established by $^{210}Pb/^{210}Bi$ after separation of the lead (Attachment 14A, "Radioactive Decay and Equilibrium"). The ingrowth of bismuth is allowed, and complexation and precipitation remove the parent, lead. Yield is determined by the addition of bismuth carrier after the ingrowth period.

The scheme is outlined here.

$$\text{Sample} \xrightarrow{\text{Ba Carrier} + H_2SO_4} (Ba/Pb)SO_4 \xrightarrow{\text{pH 4/EDTA}} [(Pb)(EDTA)]^{-2}_{aq} \xrightarrow{\text{pH } 1/H_2SO_4} PbSO_4\downarrow \xrightarrow{Na_2CO_3} \underset{\text{(ingrowth begins)}}{PbCO_3\downarrow\rightarrow}$$

$$\xrightarrow{\text{HCl + Bi carrier}} BiOCl\downarrow + Pb^{+2}$$

This represents a special exception to adding carrier. Usually, it is added at the beginning of the analysis. However, in this case, the bismuth carrier would have brought nonequilibrium bismuth through the analysis, creating an inaccuracy. Thus, adding the bismuth carrier at the end ensures maximum recovery of only the newly formed isotope.

Compiled from: Bagnall, 1957; EPA, 2000; Parsa, 1998; To, 1993.

14.11 References

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ATTACHMENT 14A
Radioactive Decay and Equilibrium

The rate of decay of a number of atoms, N_1, of a radionuclide can be expressed by Equation 14A.1, where λ_1 is (ln 2)/$t_{½}$ for the radionuclide and *t* is the time during which the change in N_1 is observed:

$$-\left(\frac{dN_1}{dt}\right)=\lambda_1 N_1 \tag{14A.1}$$

The radionuclide may decay to a stable nuclide, or to another radionuclide. In the first instance, the total number of atoms of stable nuclide formed as a result of the decay of N_1 eventually will equal N_1.

When the decay product of the original radionuclide is another radionuclide, three distinct equilibrium relationships exist between the parent and progeny based on the half-lives of the original and newly formed radionuclides. "Radioactive equilibrium" may be described mathematically by combining the decay-rate equations of two or more radionuclides to relate the number of atoms of one to any of the others. The three relationships between parent and progeny are referred to as "secular," "transient," and "no equilibrium" (Friedlander et al., 1981).

14A.1 Radioactive Equilibrium

A dynamic condition is initiated when a parent decays to a radioactive progeny. The progeny has its own decay equation, analogous to Equation 14A.1:

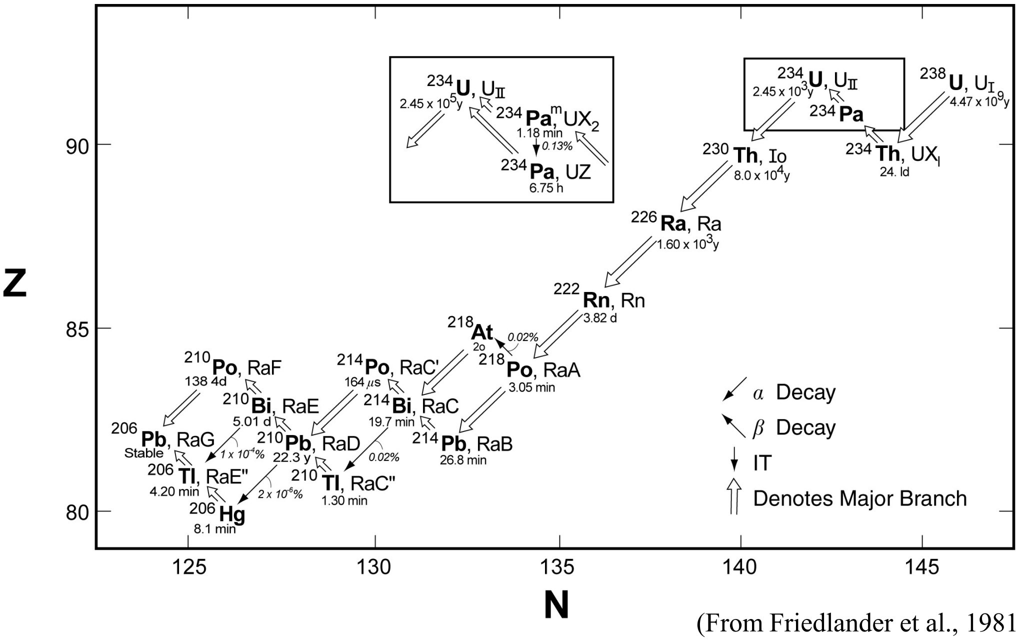
$$-\left(\frac{dN_2}{dt}\right)=\lambda_2 N_2 \tag{14A.2}$$

The relationships may become complicated if the progeny gives rise to an isotope that is also radioactive. In this case, the relationship would become, "parent–1st progeny–2nd progeny." This connection of the radionuclides is referred to as a radioactive "decay chain." When the parent of the chain is present, some number of atoms of all of the progeny in the chain eventually will be present as the predecessor radionuclides undergo radioactive decay.

14A.1.1 Secular Equilibrium

Secular equilibrium occurs when half-life of the progeny is much less than the half-life of the parent. An example, using the parent-progeny relationship between ^{210}Pb ($t_{½} \approx 22.6$ y) and ^{210}Bi ($t_{½} \approx 5$ d), can be used to demonstrate this case. (For illustrative purposes, ignore the radioactive progeny of the ^{210}Bi radionuclides).

Figure 14A.1 identifies the entire decay chain from ^{238}U, of which ^{210}Pb and ^{210}Bi are a part.



(From Friedlander et al., 1981)

FIGURE 14A.1 — Decay chain for ^{238}U

When a group of atoms of lead are isolated (e.g., radiochemical purity is achieved by precipitation), no atoms of bismuth are present at the time of isolation (t = 0). From that moment, the number of atoms of bismuth present can be described by two equations: the rate of decay of the lead and the rate of decay of the bismuth. For each atom of lead that decays, one atom of bismuth is produced. Thus a single equation can be developed to show this relationship:

$$\text{Activity of }^{210}\text{Bi} = \left[\frac{dN_2}{dt}\right] = \lambda_1 N_1 - \lambda_2 N_2 \tag{14A.3}$$

This equation can be solved to yield a relationship between the number of atoms of lead and bismuth at any time *t* after the isolation of lead. The general equation is:

$$N_2 = N_1^0 [\lambda_1/(\lambda_2 - \lambda_1)] \{ e^{-\lambda_1 t} - e^{-\lambda_2 t} \} + N_2^0 \, e^{-\lambda_2 t} \tag{14A.4}$$

Where:
N_2 = atoms of progeny (bismuth), present at any time *t*
N_1^0 = atoms of parent (lead), initially present
λ_1 = decay constant of parent
λ_2 = decay constant of progeny

N_2^0 = The number of atoms of progeny present at the time of isolation of parent.

The activity of the progeny (A_2) can then be calculated by multiplying both sides of Equation 14A.4 by λ_2:

$$A_2 = \lambda_2 N_2 = N_1^0 \, [\lambda_2 \lambda_1/(\lambda_2 - \lambda_1)]\{ e^{-\lambda_1 t} - e^{-\lambda_2 t} \} + \lambda_2 N_2^0 \, e^{-\lambda_2 t} \qquad (14A.5)$$

If radiochemical purity is ensured initially, then

$$N_2^0 = 0 \qquad (14A.6)$$

and the terms including N_2^0 in both Equations 14A.4 and 14A.5 equal zero.

Plotting this relationship as a function of time yields the graph shown in Figure 14A.2 for the ^{210}Pb-^{210}Bi radionuclides. The three significant aspects of this relationship are:

- The total activity of the sample actually increases to a maximum (until it is ≈ $2A_{Pb}$),
- The activity of the bismuth and lead are approximately equal after about seven times the half-life of bismuth, and
- The activity of bismuth decays with the half-life of lead after equilibrium has been established.

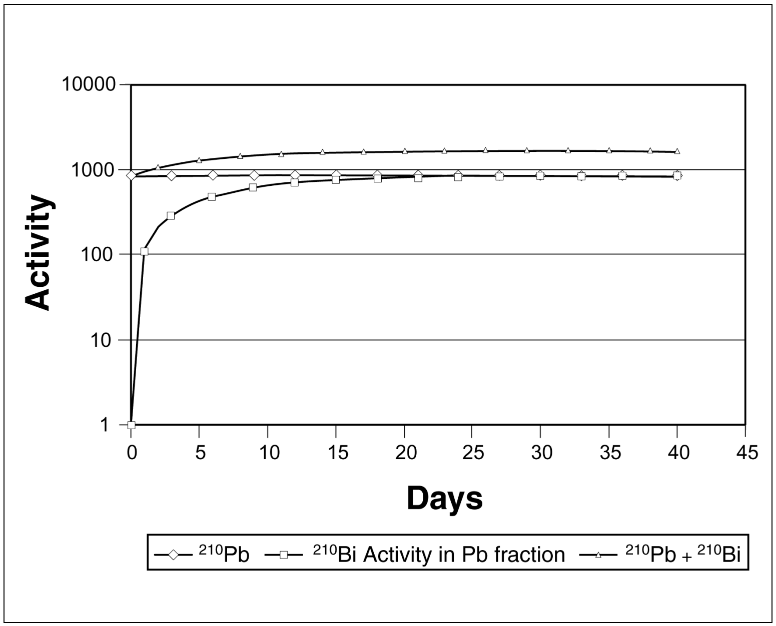


FIGURE 14A.2 — Secular equilibrium of ^{210}Pb/^{210}Bi

14A.1.2 Transient Equilibrium

Transient equilibrium occurs when the half-life of the progeny is less than the half-life of the parent. This can be demonstrated using the relationship between ^{95}Zr ($t_{½}$ ≈ 64 d) and ^{95}Nb ($t_{½}$ ≈ 35 d). Figure 14A.3 identifies the same types of relationships as were seen in the case of secular equilibrium. For transient equilibrium, the total activity passes through a maximum, and then decreases with the characteristic half-life of zirconium. Note that the activity of the niobium exceeds the activity of the zirconium after about 2 half-lives of the niobium. A significant aspect of this radioactive equilibrium that occurs at about this time is that the activity curve for the progeny reaches a maximum value. This can be determined for the general case by taking the first derivative of Equation 14A.5 and setting it equal to zero (Equation 14A.7):

$$A_{\text{maximum, progeny}} = \frac{[\lambda_1 - \lambda_2]}{[\ln\lambda_1 - \ln\lambda_2]} \qquad (14A.7)$$

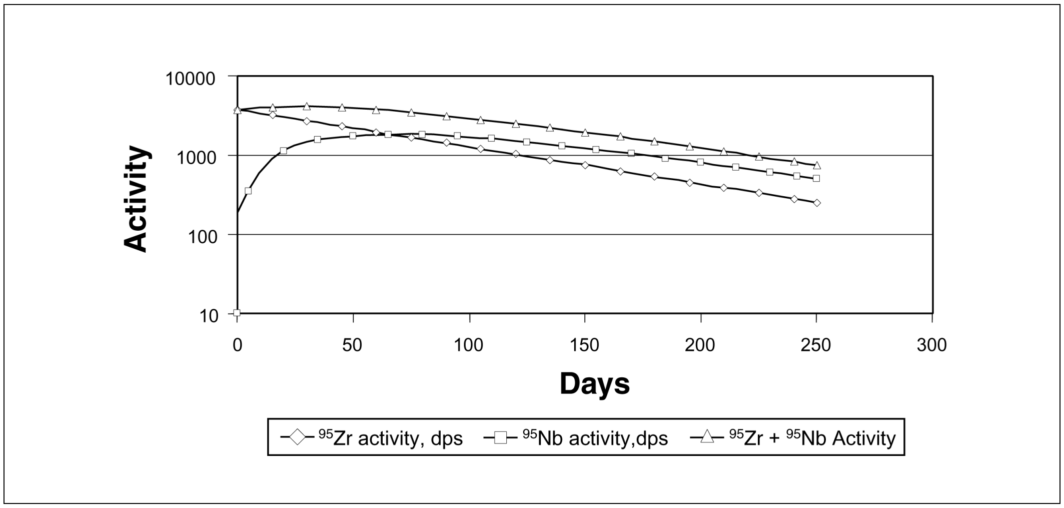


FIGURE 14A.3 — Transient equilibrium of ^{95}Zr/^{95}Nb

For the example in Figure 14A.3, this occurs at 67 days. When performing low-level analysis, knowing when this maximum activity occurs can help to achieve a lower minimum detectable amount of the progeny.

After approximately seven times the half-life of the progeny (in this case ^{95}Nb), the activity of the progeny decays with the half-life of the parent, similar to the secular equilibrium case. If the ^{95}Nb were to be separated from the parent at any time, it would decay with its own characteristic half-life.

14A.1.3 No Equilibrium

The no-equilibrium case occurs when the half-life of the progeny is greater than the half-life of the parent. Figure 14A.4 demonstrates this example for ^{239}U ($t_{½} \approx$ 23.5 min) and ^{239}Np ($t_{½} \approx$ 2.36 d $\approx$ 3,400 min). The notable characteristic here is the total activity continually decreases after time zero.

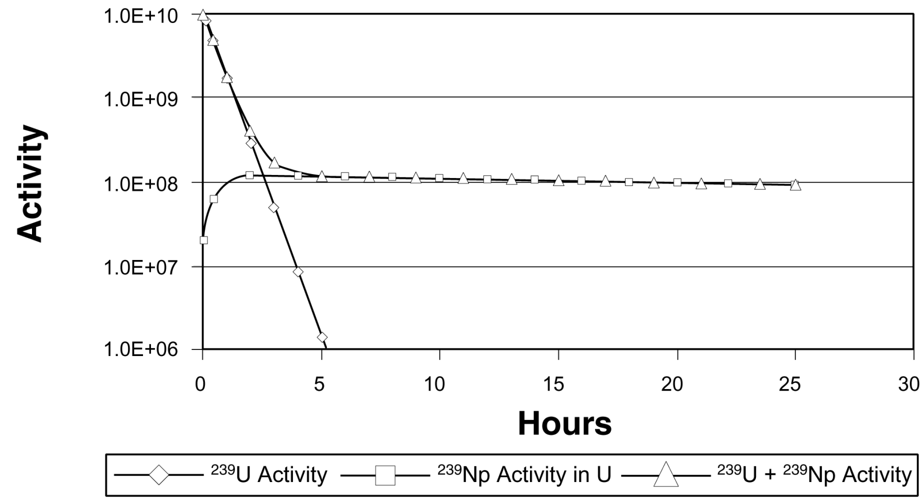


FIGURE 14A.4 — No equilibrium of $^{239}U/^{239}Np$

14A.1.4 Summary of Radioactive Equilibria

In all three cases, Equation 14A.5 is used to calculate the activity of progeny after radiochemical separation of the parent. The important aspects of the relationship (Table 14A.1) are:

- It allows the analyst to optimize when, and for how long, to count a sample in which a parent-progeny relationship exists. For the secular and transient radiochemical equilibria, if approximately seven times the half-life of the progeny has passed, then equilibrium has been established. Thus for the ^{90}Sr/Y parent-progeny pair, the time to reach maximum activity is $\approx 7\times(t_{½\ \mathrm{Yttrium}})$, or about 18 days.

- For the "transient equilibrium" case, a higher progeny activity may be achieved (relative to the parent), thus improving counting statistics for calculation of the initial parent activity.

- For the "no-equilibrium" case, if approximately seven times the half-life of the parent has passed, only progeny is left, and the activity of progeny can be related directly to the initial activity of the parent.

- It provides the analyst with important information about timing of intermediate separation steps in procedures (e.g., whether or not analysis must proceed immediately or can be set aside for a certain period of time).

TABLE 14A.1 — Relationships of radioactive equilibria

Type of Equilibrium	Relationship of Half-lives	Advantages	Other Useful Examples
Secular	Parent >> Progeny	If progeny half-life is as short as a few days, equilibrium is established in a reasonable time frame for analysis.	^{90}Sr – ^{90}Y ^{137}Cs – ^{137m}Ba ^{226}Ra – ^{222}Rn ^{228}Ra – ^{228}Ac
Transient	Parent > Progeny	If both half-lives are measured in hours to days, equilibrium activity of progeny peaks in a reasonable time frame for analysis.	^{222}Rn with its decay chain (for de-emanation analysis) ^{212}Pb – ^{212}Bi
None	Parent < Progeny	If parent half-life is a day or less, its activity contributes negligibly after a week.	^{131}Te – ^{131}I

14A.1.5 Supported and Unsupported Radioactive Equilibria

The connection between parent and progeny has one additional aspect that is significant for environmental analysis: whether or not the progeny activity is constantly "supported" by the parent in the sample. When the progeny is constantly supported, it appears to have the half-life of the parent. However, it can become unsupported, in which case it would decay with its own characteristic half-life.

For example, consider a soil sample that was contaminated with 3.7 Bq/g (100 pCi/g) of ^{232}Th ($t_{½} \approx .4 \times 10^{10}$ y). One concern about this radionuclide is the dissolution of some of its progeny into ground water: ^{228}Ra ($t_{½} \approx 5.76$ y), ^{224}Ra ($t_{½} \approx 3.66$ d) and ^{220}Ra ($t_{½} \approx 55.6$ s). Ground-water pH is normally between 6 and 8. At this pH, and with the crustal concentration of thorium/radium, the solubility of radium is significantly greater than that of thorium. As ^{228}Ra dissolves in the ground water, the ^{232}Th parent remains in the soil phase. The ground water will then migrate with the radium into wells, streams, aquifers, etc. The radium in the ground water is now "unsupported" because it is no longer in equilibrium with the decay of the thorium.

If we continue to follow the decay chain to ^{228}Th, the insolubility of thorium again "breaks" the decay chain in the ground water, because it will precipitate. However, its two progeny (^{224}Ra and ^{220}Rn) will continue to be soluble, and thus also be unsupported.

This is important when making decisions about sample shipment method and holding times prior to analytical separations. If it is assumed that the decay chain is supported, there is no reason to hasten the onset of the chemical analysis. However in the unsupported case, the half-lives of the ^{224}Ra and ^{220}Ra will affect the ability to achieve project measurement quality objectives and data quality objectives.

14A.2 Effects of Radioactive Equilibria on Measurement Uncertainty

14A.2.1 Issue

It is sometimes necessary to ensure that radionuclides have achieved radioactive equilibrium with their progeny or to establish and correct for disequilibrium conditions. This is particularly applicable for protocols that involve the chemical separation of long-lived radionuclides from their progeny, or long-lived progeny from their parents. This is also applicable for nondestructive assays like gamma spectrometry, where photon emission from progeny may be used to determine the concentration of a stable parent, or a parent which is radioactive but not a gamma emitter.

14A.2.2 Discussion

Application of Equations 14A.4, 14A.5, 14A.6 and 14A.7 can be shown by example. Radium-226 ($t_{½} \approx$ 1,600 y), is a common, naturally occurring radionuclide in the uranium series. Radium-226 is found in water and soil, typically in secular equilibrium with a series of shorter-lived radionuclides beginning with the ^{222}Ra ($t_{½} \approx$ 3.8 d) and ending with stable lead. As soon as ^{226}Ra is chemically separated from its progeny in an analytical procedure (via coprecipitation with barium sulfate), its progeny begin to re-accumulate. The progeny exhibit a variety of alpha, beta, and gamma emissions, some of which will be detected when the precipitate is counted. The activity due to the ingrowth of radon progeny should be considered when evaluating the counting data (Kirby, 1954). If analysis of radon is performed, the ingrowth of all progeny must be allowed prior to counting in order to minimize uncertainty. Examining the decay chain (Figure 14A.1) and the respective half-lives of radionuclides through ^{214}Po (for the purposes of the analysis, the progeny ^{214}Pb ends the decay chain and contributes insignificantly to the total count rate), it is appropriate to wait about 3 or 4 hours. In some cases, it may be necessary to derive correction factors for radioactive ingrowth and decay during the time the sample is counting. These factors are radionuclide-specific and should be evaluated for each analytical method.

Radioactive equilibrium concerns also apply to non destructive assays, particularly for uranium and thorium series radionuclides. Important radionuclides in these series (e.g., ^{238}U and ^{232}Th) have photon emissions that are weak or otherwise difficult to measure, while their shorter-lived primary, secondary or tertiary progeny are easily measured. This allows for the parents to be quantified indirectly—i.e., their concentration is determined by measuring their progeny and accounting for the length of time between separation of parent and progeny.

When several radionuclides from one decay chain are measured in a sample, observed activity ratios can be compared to those predicted by decay and ingrowth calculations, the history of the sample and other information. For example, undisturbed soil typically contains natural uranium with approximately equal activities of ^{238}U and ^{234}U, while water samples often have very different ^{238}U/^{234}U ratios. Data from analysis of ores or materials involved in processing that could disrupt naturally occurring relationships (i.e., selectively remove elements from the material) require close attention in this regard.

All numerical methods (electronic and manual) should be evaluated to determine if the appropriate correction factors related to equilibrium concerns have been used. This includes a check of all constants used to derive such correction factors, as well as the use of input data that unambiguously state the time of all pertinent events (chemical separation and sample counting). A specific example is ^{228}Ra analysis with ingrowth of ^{228}Ac. The actinium is separated from the radium after a measured time and is immediately counted. The half-life of actinium is used to correct for the decay of actinium atoms during the counting interval and for the time interval since the separation from radium. Equation 14A.4 is used to calculate the atoms of radium, based on the number of atoms of actinium, at the time of separation of actinium from radium. The half-life of radium is used to calculate the radium activity and decay-correct from the sample preparation time back to the time of sample collection as follows:

$$N_B = N_c/[\varepsilon][1\text{-}\mathrm{EXP}(-\lambda_{Ac}t_c)]$$

and

$$N_0 = N_B\ \{\mathrm{EXP}(+\lambda_{Ac}t_s)\}$$

Where:

N_c is the number of counts accumulated during the counting interval
N_B is the number of atoms of actinium at the beginning instant of the count interval
N_0 is the number of atoms of actinium decay corrected back to the time of separation from Ra
λ_{Ac} is the decay constant for actinium
ε is the detector efficiency
t_c is the counting interval (clock time)
t_s is the time between separation of actinium from radium to the start of the count interval.

Equation 14A.4 is then used to calculate the atoms of radium based on the number of atoms of actinium that exist at the time actinium is separated from radium. The half-life of radium is used to calculate the radium activity and decay-correct from the sample preparation time back to the time of sample collection.

Samples requiring progeny ingrowth should be held for sufficient time before counting to establish equilibrium. Limits for minimum ingrowth and maximum decay times should be established for all analytical methods where they are pertinent. For ingrowth, the limits should reflect the minimum time required to ensure that the radionuclide(s) of interest has accumulated sufficiently to not adversely affect the detection limit or uncertainty. Conversely, the time for radioactive decay of the radionuclides of interest should be limited such that the decay factor does not elevate the minimum detectible concentration or adversely affect the measurement uncertainty.

Samples where equilibrium is incorrectly assumed or calculated will produce data that do not represent the true sample concentrations. It is difficult to detect errors in equilibrium assumptions or calculations. Frequently, it takes anomalous or unanticipated results to identify these errors. In these cases, analysts need to know the sample history or characteristics before equilibrium errors can be identified and corrected. Some samples may not be amenable to nondestructive assays because their equilibrium status cannot be determined; in such cases, other analytical methods are indicated.

14A.2.3 Examples of Isotopic Distribution – Natural, Enriched, and Depleted Uranium

Isotopic distribution is particularly important with respect to uranium, which is ubiquitous in soils and is also a contaminant in many site cleanups. The three predominant uranium isotopes of interest are ^{238}U, ^{234}U, and ^{235}U, which constitute 99.2745, 0.0055, and 0.72 atom-percent, respectively, of natural uranium[2], i.e., uranium as found in nature (Parrington et al., 1996). The ratio of ^{238}U to ^{234}U in undisturbed uranium deposits will be the same as the ratio of 99.2745/0.0055 = 18,050, because all the ^{234}U comes from the decay of ^{238}U (^{234}U originally present when the Earth was formed has long since decayed).

However, human activities related to uranium typically involve changing the ratio of natural uranium by separating the more readily fissionable ^{235}U from natural uranium to produce material "enriched" in ^{235}U, for use in fuel cycle and nuclear weapons related activities. Typical ^{235}U enrichments range from 2 percent for reactor fuels to greater than 90 percent ^{235}U for weapons. The enrichment process produces material that is called "DU," or depleted in uranium (i.e., the uranium from which the ^{235}U was taken[3]). The enrichment process also will disrupt the ^{234}U content, which will change the $^{238/234}$U ratio from what is occurring naturally (i.e., 18,050). While the ^{235}U concentrations of depleted uranium are reduced relative to natural ores, they still can be measured by several assay techniques. This gives rise to uranium with three distinct distributions of ^{238}U,^{235}U, and ^{234}U, referred to as "natural," "enriched," and "depleted" uranium. Because ^{238}U,^{235}U, and ^{234}U are alpha emitters with considerably different half-lives and specific activity, a measurement of a sample's total uranium alpha activity cannot be used to quantify the sample's isotopic composition or uranium mass without knowing if the uranium is natural or has been enriched or depleted in ^{235}U. However, if this information is known, measurement and distribution of the sample's uranium alpha activity can be used to infer values for a sample's uranium mass and for the activities of the isotopes ^{238}U, ^{235}U, and ^{234}U. This ratio can be determined directly or empirically using mass or alpha spectrometry, techniques that are time- and cost-intensive, but which provide the material's definitive isotopic distribution. It is often

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[2] The natural abundance of ^{235}U of 0.72 atom-percent is a commonly accepted average. Actual values from specific ore samples vary.

[3] Enriched and depleted refer primarily to ^{235}U.

practical to perform mass or alpha spectrometry on representative samples from a site to establish the material's isotopic distribution, assuming all samples from a given area are comparable in this respect. Once established, this ratio can be applied to measurements of uranium alpha activity to derive activity concentrations for ^{238}U, ^{234}U, and ^{235}U data.

14A.3 References

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