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Part I

**ANALYTICAL CHEMISTRY OF ELEMENTS STUDIED  
ON THE MANHATTAN PROJECT**



## Chapter 1

### URANIUM

By C. J. Rodden and J. C. Warf\*

In this chapter the methods for separating and determining uranium are discussed, and procedures are described. Because of the unique importance of uranium and its compounds, a section on basic chemical properties of this element is included. Methods of dissolving uranium metal and its compounds are discussed and methods of separation are given.

The most lengthy part of the chapter consists of detailed discussions of the gravimetric, volumetric, colorimetric, and fluorometric methods of determination and specific laboratory procedures.

#### 1. THE CHEMISTRY OF URANIUM AND ITS COMPOUNDS<sup>1</sup>

**1.1 Introduction.** A great variety of minerals and ores contain uranium, and these are widespread in geographical distribution. As a source of uranium the two most important minerals are pitchblende and carnotite. Pitchblende,  $U_3O_8$ , is of igneous origin and contains variable amounts of other elements, whereas carnotite is a sedimentary mineral of granitic origin and contains potassium, vanadium, and uranium in the proportions approximately represented by the formula  $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$ . Carnotite usually occurs in sandstone admixtures.

\*Special acknowledgment is made to the following for their contributions to sections with which they were identified: Sec. 1.4, "Complex Formation," J. F. Flagg; Sec. 2.2, "Precipitation," N. H. Furman; Sec. 3.2, "Gravimetric Methods," N. H. Furman; Sec. 3.3, "Volumetric Methods," M. S. Richmond; Sec. 3.5, "Fluorometric Methods," Forrest Clark. Acknowledgment is also made to C. C. Casto, D. P. Krause, H. F. Priest, L. B. Rogers, R. H. Smellie, D. H. Templeton, and J. I. Watters.

Uranium metal has a melting point of approximately 1130°C and a density of 18.95. It may be machined, hot-drawn, and cold-worked. The surface takes a high polish but slowly tarnishes in air.

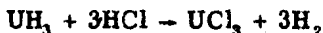
Uranium forms intermetallic compounds with most other metals; these include iron, lead, and mercury. The metal, which lies near beryllium or aluminum in electropositivity, is a strong reducing agent, and it forms binary compounds with most other elements. In the dry state compounds in which the valence of uranium is +3, +4, +5, or +6 are well known. However, in aqueous solution, uranium(V) disproportionates into uranium(IV) and uranium(VI), whereas the strong reducing agent uranium(III) is rapidly oxidized by dissolved oxygen and also slowly reduces water to liberate hydrogen. Uranium(VI), the most stable form in aqueous solution, usually exists in, and is separated from, acidic or neutral solutions as the uranyl ion,  $[\text{UO}_2]^{++}$ . Uranium(VI) often separates from alkaline solutions as the diuranate,  $[\text{U}_2\text{O}_7]^{--}$ , as, for example,  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ . It may also separate as the uranate,  $[\text{UO}_4]^{--}$ , as, for example,  $\text{Na}_2\text{UO}_4$ . Variable amounts of hydrous oxide may also be present in such precipitates.

The common uranyl salts as well as their solutions are brilliant yellow in color. Uranium(IV) salts and their solutions are deep green by reflected light. Trivalent uranium salt solutions are reddish purple, although the solid crystals may be olive-green, reddish brown, or black depending on the crystal size. The uranium (VI)/(IV) couple exhibits the Becquerel effect, in which the potential of the electrode increases with illumination. The photochemical reduction of the uranyl ion to the uranium(IV) ion by organic compounds has been the subject of considerable research.

The uranyl ion exhibits a green-yellow fluorescence, which is weak in aqueous solution but strong in the crystalline state.

Important binary compounds include the hydride, carbides, nitrides, oxides, and halides.

The hydride, a pyrophoric dark-gray powder, is formed by the action of hydrogen on the metal at 250°C at atmospheric pressure. Uranium hydride serves as a starting material for the preparation of many compounds. For example, uranium trichloride is readily prepared by the action of hydrogen chloride.



Decomposition of the hydride leaves the finely divided metal in an exceedingly reactive state. The hydride forms "amalgams" of various compositions, some of which are semisolids.

The three carbides, UC,  $\text{U}_2\text{C}_3$ , and  $\text{UC}_2$ , form high-melting crystals of metallic luster.



The nitrides, UN and others with composition between  $UN_{1.5}$  and  $UN_{1.8}$  (depending on the temperature), are unreactive dark powders. The UN is not decomposed when heated to  $2500^{\circ}\text{C}$  in an inert crucible at low pressures.

The common oxides of uranium are  $UO_2$ , a dark-brown powder called "brown oxide";  $U_3O_8$ , ordinarily a black but sometimes an olive-green powder, called "black oxide"; and  $UO_3$ , the color of which varies from red to yellow, depending on the crystal modification. Uranium peroxide,  $UO_4 \cdot 2H_2O$ , which is yellow, can be precipitated in slightly acidic solution by hydrogen peroxide. It dissolves in alkalis, yielding peruranates. Hydrous uranyl oxide,  $UO_3 \cdot H_2O$ , dissolves easily in acids, and  $UO_3$  and  $U_3O_8$  are soluble in nitric acid.

There are five fluorides of uranium— $UF_3$ , a black-colored salt;  $UF_4$ , a difficultly soluble compound, commonly called "green salt";  $U_2F_9$ , which is black;  $UF_5$ , a white substance; and  $UF_6$ , a colorless compound, which is readily volatile (b.p.  $56.4^{\circ}\text{C}$ ).  $UF_4$  and  $UF_6$  are important compounds of uranium. The latter is readily hydrolyzed by water, forming uranyl fluoride. The tetrafluoride is usually prepared from the dioxide and anhydrous hydrogen fluoride at  $500$  to  $600^{\circ}\text{C}$ .

Uranium forms four chlorides— $UCl_2$ , which is olive-green;  $UCl_3$  and  $UCl_4$ , which are green; and  $UCl_5$ , which is yellow. The trichloride forms a wine-red unstable solution, and the tetrachloride forms a clear green solution in water. On dissolving in water the pentachloride disproportionates, forming uranium(IV) and uranium(VI), whereas the hexachloride hydrolyzes to  $UO_2Cl_2$ . The two higher chlorides are volatile and unstable; the tetrachloride can be sublimed at  $550$  to  $600^{\circ}\text{C}$ . The tribromide and tetrabromide, triiodide and tetraiodide, and mixed halides are known.

The most common uranyl salts, namely, the nitrate, sulfate, chloride, acetate, and perchlorate, are soluble yellow-colored salts. The diuranates, such as  $(NH_4)_2U_2O_7$  and  $Na_2U_2O_7$ , are insoluble. Various uranium(IV) salts such as the sulfate, chloride, bromide, and oxalate are readily prepared. Most of the uranyl and uranium(IV) salts form several hydrates.

Uranyl nitrate is of particular importance because, although highly ionized, it can be extracted from a concentrated nitrate solution by organic solvents such as ether. Advantage is taken of this unique property in the separation or purification of uranium.

**1.2 Valence States.** The oxidation potentials of the principal valence states of uranium, namely, uranium(III), uranium(IV), and uranium(VI), as well as the transitory uranium(V), are discussed in Chap. 25 on "Electrometric Methods." Owing to the relatively low oxidation potential of the uranium (VI)/(IV) couple, the element can be quantitatively converted to either valence state at will. The alter-

nate use of both valence states permits many separations not otherwise possible. An important application is the use of cupferron, which forms an extractable precipitate with uranium(IV). Other cupferrates may first be separated from the oxidized solution, and then uranium(IV) cupferrate may be precipitated alone after reduction. The same principle is sometimes used in precipitation with oxalic acid. Uranium(IV) oxalate is insoluble, but uranyl ion forms a soluble complex with oxalic acid. Titrations usually involve a prereduction to uranium(IV) followed by an oxidation titration to uranium(VI). The instability of uranium(III) has not permitted the use of this valence state in quantitative analysis.

Acidified uranyl salt solutions are readily reduced by a number of metals or their amalgams, including zinc, aluminum, magnesium, cadmium, bismuth, silver, and copper. In most cases the uranium is reduced to a mixture of the trivalent and quadrivalent states; the proportion of the former ranges up to 40 per cent of the total uranium.<sup>2</sup> Reduction of acidic chloride solutions with silver yields only the quadrivalent form. Uranyl solutions may also be reduced electrolytically to mixtures of uranium(IV) and uranium(III). Under the proper conditions tin(II) chloride, titanium(III) salts, and sodium hyposulfite reduce uranyl salts.

Trivalent uranium is a powerful reducing ion; exposure to air for a few minutes serves to oxidize it quantitatively to the quadrivalent state. Uranium(IV) solutions are relatively stable in the presence of air. When warmed to 60 to 80°C or when shaken with oxygen, they are oxidized more rapidly. Uranium(IV) in solution is converted to uranium(VI) by most of the common oxidizing agents.

A detailed description of uranium and its compounds is given in "Uranium Chemistry," National Nuclear Energy Series, Division VIII, Volume 5.

**1.3 Solution of Uranium and Its Compounds.** The method to be selected for the solution of metallic uranium, its alloys, or its compounds depends on the nature of the sample, the constituent to be determined, and the method of analysis. Nitric acid is often employed because it dissolves all or nearly all compounds and alloys of uranium. The presence of nitrates, however, cannot be tolerated in many procedures, such as the volumetric determination following a reduction by zinc. A general discussion of available methods of solution appears below. Methods for dissolving ores and rocks will be found under Sec. 4 of this chapter.

(a) **Uranium and Its Alloys** The pure metal dissolves in nitric acid at a moderate rate and forms uranyl nitrate. Uranium turnings, sintered or pressed powder, or other forms with a large surface area,

may be oxidized explosively by nitric acid. For this reason, when large quantities are to be dissolved, only small portions (3 to 6 g at a time) should be added to the acid. The use of insufficient nitric acid in the solution results in the formation of traces of hydrazine or other intermediates<sup>3</sup> that can be destroyed by oxidation with dichromate or permanganate.<sup>4</sup>

Uranium reacts extremely rapidly with 12N HCl. In 6N acid the reaction is still rapid, but 2N acid attacks the metal slowly. The reddish-violet color of trivalent uranium chloride is visible shortly after the reaction begins, but it is soon masked by a black precipitate that has a tendency to remain in suspension. The proportion of the uranium that is converted to the insoluble precipitate varies from 0.1 to 20 per cent, depending on the acid concentration, ratio of acid to metal, time of reaction, and temperature.<sup>5,6</sup> The resulting mixture of black precipitate and uranium trichloride and tetrachloride can be oxidized to a clear uranyl solution by nitric acid, hydrogen peroxide, bromine water, or perchloric acid. With perchloric acid the solution must be boiled to fumes. Hydrochloric acid containing traces of fluosilicic acid dissolves uranium without the formation of the black precipitate, producing green uranium(IV) chloride.<sup>7</sup>

Dilute sulfuric acid has little effect on uranium. Addition of an oxidizing agent such as hydrogen peroxide causes a slow reaction. The metal can also be dissolved anodically in sulfuric acid by using a current of 1.5 amp and a potential of about 3 volts.<sup>8</sup> The action of dilute perchloric acid on uranium is comparable to that of sulfuric acid in that there is scarcely any reaction except in the presence of oxidizing agents such as peroxides or chlorates. When perchloric acid is boiled down to fumes in the presence of uranium, an extremely vigorous and probably dangerous reaction takes place, during which sparks are observed.

Cold 85 per cent phosphoric acid attacks uranium slowly, but after the acid is concentrated by boiling, a fairly rapid reaction occurs. With an excess of acid a green solution of uranium(IV) phosphate is obtained which gives a gelatinous precipitate on dilution. A glassy substance, which is extremely difficult to redissolve, is formed when the solution is boiled down too far. The solution of uranium in phosphoric acid is accelerated by oxidizing agents such as nitric acid or peroxides, or by anodic oxidation.

Organic acids are in general without effect on uranium except in the presence of hydrogen chloride as a catalyst. Thus glacial acetic acid reacts to yield uranium(IV) acetate if hydrogen chloride is bubbled in, or if a little hydrochloric acid is added.<sup>9</sup>

Alkaline solutions of peroxides dissolve uranium and many of its compounds, forming peruranates.<sup>10</sup>

The reduction of heavy metal salts, such as mercuric nitrate, silver nitrate, stannous chloride, and platinum chloride, in aqueous solution by uranium was observed in 1882 by C. Zimmermann.<sup>11</sup> Silver sulfate solution reacts slowly with the metal. Silver perchlorate reacts vigorously, resulting in the formation of silver, silver chloride, and uranyl perchlorate.<sup>12,13</sup> Cupric ammonium chloride or acetate dissolves uranium without permanent precipitation of metal.<sup>14,15</sup>

The alloys of uranium can usually be dissolved as readily as uranium metal itself. Some alloys, however, are more readily dissolved; for example, uranium-lead and uranium-bismuth alloys react with water. Uranium-copper, uranium-zinc, and other alloys dissolve readily in nitric acid, but the tin alloy reacts, leaving a precipitate of hydrated stannic oxide. The columbium, tantalum, and tungsten alloys require special treatment. The nature of the alloying metal usually suggests the proper method of solution, and difficulties at this stage are rarely encountered.

(b) Uranium Oxides: Uranates. Nitric acid dissolves all the normal oxides of uranium— $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$ ,  $\text{UO}_3$ —with the formation of uranyl nitrate. Uranium peroxide,  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ , is readily dissolved in an acidic reducing solution; in hydrochloric acid, uranyl chloride and chlorine are formed. The uranates, diuranates, and uranium trioxide dissolve in the common acids. Neither  $\text{UO}_2$  nor  $\text{U}_3\text{O}_8$  dissolves in dilute hydrochloric or sulfuric acid at a practical rate.<sup>16,17</sup> Each is slowly oxidized by long heating with sulfuric acid, forming uranyl sulfate. The oxides are readily dissolved by fuming with perchloric acid, which results in the formation of uranyl perchlorate. Soluble peruranates are obtained by treatment of uranium oxides with alkaline peroxides.<sup>10,18</sup>

(c) Uranium Fluorides. Uranyl fluoride and uranium hexafluoride are soluble in water. The latter is violently hydrolyzed, forming uranyl fluoride and hydrofluoric acid. Uranium pentafluoride disproportionates and hydrolyzes in water to form hydrofluoric acid, soluble uranyl fluoride, and insoluble uranium(IV) fluoride. Uranium(IV) fluoride and uranium(III) fluoride are both insoluble in water.

Uranium fluorides are often converted into  $\text{U}_3\text{F}_8$  prior to their solution. This conversion can be accomplished by hydrolysis with steam<sup>19</sup> or fusion with boric acid,<sup>20</sup> ammonium oxalate,<sup>21</sup> or potassium pyrosulfate.<sup>22</sup> Uranium tetrafluoride can be readily converted to  $\text{U}_3\text{F}_8$  by ignition in air<sup>23</sup> or by heating with ammonium carbonate<sup>45,7</sup> and then dissolved as above. Uranium tetrafluoride is readily dissolved by boric acid solutions that have been acidified with sulfuric, hydrochloric, or perchloric acid, giving uranium(IV) sulfate, chloride, or perchlorate. When a mixture of nitric and boric acids is used uranyl nitrate and fluoboric acid are formed. Ferric iron oxidizes  $\text{UF}_4$  to

uranyl compounds and forms a complex with the fluoride ion. Aluminum chloride dissolves  $UF_4$  by complexing the fluoride ion.<sup>24</sup> Neutral oxalate solutions dissolve uranium tetrafluoride owing to the stability of the uranium(IV) oxalate complex in neutral mediums. Strongly acidic solutions of ceric sulfate oxidize uranium tetrafluoride to uranyl fluoride. Alkaline peroxides dissolve uranium tetrafluoride and form peruranates. Uranium tetrafluoride is readily dissolved by fuming perchloric acid to form uranyl perchlorate; the hydrofluoric acid is expelled. Long boiling with nitric acid causes slow solution of uranium tetrafluoride, and heating with phosphoric acid results in the formation of uranium(IV) phosphate and removal of the fluorine. Hot concentrated sulfuric acid reacts to form a sulfate that dissolves on dilution with water. However, the fluorine is not quantitatively expelled. Treatment with dilute sulfuric acid and powdered quartz yields fluosilicic acid and uranous sulfate. Uranium trifluoride undergoes reactions similar to those of the tetrafluoride with the exception that the trifluoride is not soluble in neutral oxalates.

(d) Other Uranium Compounds. Since uranium chlorides, bromides, and iodides either dissolve in water or react with water, their solution is generally simple. Uranium carbides dissolve on prolonged boiling with nitric acid but are usually oxidized by air or oxygen to  $U_3O_8$  before solution. Uranium sulfates, acetates, and many other salts are soluble in water.

1.4 Complex Formation. Uranium forms compounds that may be classified as double salts. The element also forms compounds that are definitely "complex." Many of these are of the "inner complex" or "chelate" type.

There are a great many good analytical data available on the composition of many of the uranium complex compounds. There is still a lack of definite evidence for the formulas for some of the complex ions in solution. Consequently, considerable caution must be observed in the interpretation of the formulas of uranium complexes for which the evidence is still indefinite.

The importance of complex ions in the analytical chemistry of uranium lies in their solubility, making them useful in separations, or in their color, making them useful in colorimetric determinations. Some different types of uranium complexes are cited in the following sections to indicate the general nature of the complex-forming power of the uranium atom.

(a) Inorganic Complexes of Uranium(VI). Many complexes of the uranyl ion with inorganic substances are known. Among the halide complexes are found the crystalline salts of fluorides such as  $[UO_2F_3]^-$ ,  $[UO_2F_5]^{-3}$ , and  $[UO_2F_6]^{-4}$ . The formation of complexes of this type may

depend, among other things, on the ratio in which the components are mixed. Salts of the chloride anion,  $[\text{UO}_2\text{Cl}_4]^{--}$ , are also known, and similar complexes with the other halides probably exist.

The nitrate ion forms complexes with the uranyl ion; crystalline ammonium derivatives and potassium derivatives of  $[\text{UO}_2(\text{NO}_3)_3]^-$  and  $[\text{UO}_2(\text{NO}_3)_4]^{--}$  are known.

The sulfate ion forms complexes in which either two or three sulfate ions are attached to a single uranyl ion. Disulfates of potassium,  $\text{K}_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , and also of organic bases such as ethylene diamine and guanidine are known. The trisulfate series includes compounds such as  $\text{Na}_4\text{UO}_2(\text{SO}_4)_3$ . The sulfate complex apparently inhibits the precipitation of  $\text{UO}_2$  at a pH of 1.5; the amount of interference is roughly a linear function of the sulfate concentration when the ratio of sulfate to uranyl is greater than 1.<sup>25</sup> Sulfate ion also reduces the solubility of uranyl nitrate in ether, which may be a related effect.<sup>26</sup>

The carbonate complexes, formed by action of ammonium or alkali carbonates or bicarbonates on uranyl hydroxide, alkali uranates, etc., are well known and have been used for many years in analyses of uranium-bearing material.<sup>27</sup> Three molecules of carbonate are associated with each molecule of  $\text{UO}_2$ , and the complex is an anion of the form  $[\text{UO}_2(\text{CO}_3)_3]^{-4}$ . However, when ammonium diuranate is dissolved in ammonium carbonate, a slight excess of carbonate over the theoretical three molecules is required.<sup>28</sup> Although the ammonium salt of the complex is soluble, the barium salt,  $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3$ , is insoluble.<sup>29</sup>

Ammonium diuranate cannot be precipitated from ammoniacal carbonate solution by ammonium hydroxide; however, sodium diuranate can be precipitated completely from carbonate solution by sodium hydroxide. Ammonium diuranate dissolves in ammonium carbonate at about pH 7.4; if this solution is treated with hydrochloric acid, however, a precipitate of ammonium diuranate appears at pH 5.2.<sup>28</sup>

Polarographic studies indicate that the same complex of the uranyl ion is present in both carbonate and bicarbonate mediums.<sup>30</sup> Electrical transport data lead to the same conclusion. These same studies also indicate qualitatively that the carbonate complex is more stable than the acetate complex, because the half-wave potential for the reduction of uranium(VI) is shifted to more negative values in carbonate or bicarbonate mediums than in the presence of acetate.

Use is made of the solubility of ammonium diuranate in ammonium carbonate in many recovery and separation reactions, particularly in the presence of iron (see references 28 and 31 to 33).

Other complexes of the uranyl ion include the cyanide,  $[\text{UO}_2(\text{CN})_4]^{--}$ , which has been shown by conductance measurements to exist as such

in aqueous solution. In the solid state  $K_2UO_2(CN)_4$  is known.<sup>34</sup> Complex amines of  $UO_2F_2$ ,  $UO_2Cl_2$ ,  $UO_2SO_4$ , and  $UO_2(NO_3)_2$  are known in which from two to six molecules of ammonia are held per atom of uranium. Hydroxylamine prevents the precipitation of ammonium diuranate in the separation of uranium and beryllium (or thorium).<sup>35,36</sup> This may be taken as an indication of the complex formation between the hydroxylamine and the uranyl ion. Hypophosphate and pyrophosphate form soluble complexes with uranyl salts,<sup>37-39</sup> giving compounds such as  $Na_2[UO_2(HPO_3)_2]$  and  $Na_2[UO_2(P_2O_7)]$ . Phosphate ion, like sulfate, prevents the quantitative extraction of uranium with ether from strong nitrate solutions.<sup>40,41</sup>

Many of the inorganic complexes are of limited interest with regard to the analytical chemistry of the uranyl ion, but their existence should be noted and considered in work involving ionic species, for example, in spectrophotometry and in solvent extractions. In such cases equilibria between simple and complex ions may be important.

(b) Organic Complexes of Uranium(VI). Literally hundreds of organic complexes of uranium salts are known; survey reports have been made.<sup>42-46</sup> Among the important uses of these complexes are colorimetric determinations of uranium, prevention of precipitation, and extraction from aqueous solution.

(1) Complexes of Aliphatic Acids. Acetate ion forms a complex with the uranyl ion in which three acetate groups are bound to one uranyl ion; the complex is anionic. The complex is not stable at low pH presumably because hydrogen ion is more firmly bound to acetate than is uranyl ion.<sup>47</sup> Other aliphatic acids (formic, butyric, etc.) form similar complexes of the type  $[UO_2(O_2CR)_3]^-$ , where R is an aliphatic radical.

Oxalate ion also forms a uranyl complex sufficiently stable to prevent precipitation of the rare-earth oxalates. In order to precipitate lanthanum oxalate from solutions that contain a uranyl salt, it is necessary to add sufficient oxalate to complex all the uranium before the lanthanum oxalate begins to precipitate.<sup>48</sup>

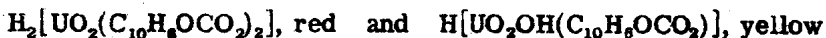
Tartrate, citrate, and malate ions also form complexes that are stable at a high pH. The uranyl tartrate complex contains one molecule of tartrate per uranium atom, as does the malate complex. Both complexes are anionic, and examples of salts<sup>49,50</sup> are  $K[UO_2OH(C_4H_4O_6)]$  and  $Na[UO_2OH(C_4H_4O_6)] \cdot 2H_2O$ . Both citrate and tartrate ions prevent precipitation of ammonium diuranate by ammonia. The citrate complex is important in uranium-poisoning therapy.

(2) Complexes of Aromatic Acids. Benzoate ion, like acetate, forms a complex anion of the type  $[UO_2(C_6H_5CO_2)_3]^-$ , of which the ammonium salt is known in the crystalline form. The hydroxybenzoic acids, especially salicylic acid, form numerous complexes, which have been

rather carefully studied. Salicylic acid forms two series of complexes, a yellow series and a red series that contain, respectively, two and three molecules of salicylic acid per atom of uranium. The complexes exist in solution or may be precipitated as insoluble pyridine, aniline, piperidine, and other salts.<sup>51</sup> Aniline salts of the disalicylate series and the trisalicylate series have been made. The salicylate complexes find use in analytical procedures as colorimetric reagents or as agents to prevent the precipitation of uranium with the rare-earth oxalates.<sup>52,53</sup>

Both *p*-hydroxy and *m*-hydroxybenzoic acids form complexes containing three molecules of acid per atom of uranium; aniline, pyridine, and other salts are known.<sup>50</sup> Cresotinic acid (2-hydroxy-3-methylbenzoic acid) forms an orange-red complex used in colorimetric analysis.<sup>54</sup>

With *o*-hydroxynaphthoic acid, complexes of this type are formed:<sup>55</sup>



Protocatechuic acid (3,4-dihydroxybenzoic acid) forms complexes of which the guanidine salts have been made. Excess sodium hydroxide is reported to cause no precipitation of uranium from these complexes. Complexes with gallic acid (3,4,5-trihydroxybenzoic acid) are also alkali-stable, and strongly colored, and they may be used for the colorimetric estimation of the uranyl ion.<sup>56,57</sup> The complex with sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) is also colored and is useful in colorimetric determinations.<sup>58</sup>

(3) Other Organic Complexes. Aromatic polyhydroxy compounds such as catechol and pyrogallol also form colored complexes with the uranyl ion.<sup>59,60</sup> Some are orange-yellow in color, and a few are red or violet.

Uranyl salts form complexes with disubstituted dithiocarbamic acid,  $\text{RR}'\text{NCSSH}$ , which are soluble in benzene and other nonpolar solvents.<sup>420a</sup> The diethyl derivative is extracted with benzene in the analysis of uranium in thorium.<sup>51</sup> The ethyl phenyl derivative acts in the same manner. Both complexes are readily formed at pH 2.8 or 3.0.

Many other extractable uranyl complexes are known. These include the chelate complexes formed with isatin- $\beta$ -oxime, quinaldic acid, 8-hydroxyquinoline, 1-nitroso-2-naphthol, and antipyrine. These compounds are insoluble in water and generally insoluble in very weakly acidic or basic solution, but they dissolve readily in such solvents as chloroform, methyl isobutyl ketone, and amyl alcohol. Such complexes are essentially neutral molecules, as contrasted with the soluble ionic type complex formed by the hydroxy acids. Complexes of 1,3-diketones with uranyl salts are also known.<sup>62,63</sup>



(c) Inorganic Complexes of Uranium(IV). The uranium(IV) ion also forms many complexes, among them complexes of the halide, sulfate, sulfite, carbonate, and phosphate ion.

Of the halide complexes,  $[\text{UF}_5]^-$  and  $[\text{UOF}_3]^-$  are known in the form of potassium and ammonium salts, and  $[\text{UCl}_6]^{--}$  is known in the form of sodium and lithium salts. Complex sulfate ions are  $[\text{U}(\text{SO}_4)_4]^{-4}$  and  $[\text{U}(\text{SO}_4)_3]^{--}$ . The sulfite complexes include two well-characterized compounds,  $(\text{NH}_4)_4[\text{U}(\text{SO}_3)_4]$  and  $\text{Na}_8[\text{U}_2(\text{SO}_3)_7] \cdot 20\text{H}_2\text{O}$ . The former resembles the oxalate as well as the sulfate complexes.<sup>64</sup> Phosphate complexes include salts<sup>65,66</sup> of the ion  $[\text{U}(\text{PO}_4)_2]^{--}$ .

(d) Organic Complexes of Uranium(IV). The uranium(IV) ion forms complexes with many of the same organic compounds that also combine with the uranyl ion. Oxalate, for example, forms a stable, soluble complex of the type  $(\text{NH}_4)_4\text{U}(\text{C}_2\text{O}_4)_4$  in neutral solutions. Acidification causes uranium(IV) oxalate to precipitate, and the addition of ammonium hydroxide results in precipitation of uranium(IV) hydroxide or the hydrated oxide. An acetate complex of the uranium(IV) ion may also exist, since uranium(IV) oxalate is soluble in solutions of ammonium acetate. However, the solution of uranium(IV) oxalate in ammonium acetate may occur simply because ammonium acetate buffers the solution to about pH 7, at which pH uranium(IV) oxalate is soluble.

Among the salts formed by the carbonate complexes are those with guanidine.<sup>64</sup>

The hydroxy acids such as tartaric, malic, quinic, citric, lactic, and glycolic form complexes with the uranium(IV) ion.<sup>67,68</sup> Some of these, such as citric acid, prevent precipitation of uranium when the solution is made basic with ammonium hydroxide. The polyhydric phenols such as catechol also form alkali-stable uranous compounds.<sup>64,69</sup> The complex ion, of which ammonium, potassium, guanidinium, pyridinium, and other salts are known, is  $[\text{U}_2(\text{C}_6\text{H}_4\text{O}_2)_7]^{-6}$  or  $[\text{U}(\text{C}_6\text{H}_4\text{O}_2)\text{OH}]^-$ . The first complex ion may also be regarded as a dimer of the ion  $[\text{U}(\text{C}_6\text{H}_4\text{O}_2)_3]^{--}$  after a seventh molecule of pyrocatechol is added.

Uranium(IV) salicylate is slightly soluble in water and readily soluble in organic solvents, as is uranium(IV) acetylacetonate. Other uranium(IV) complexes of the diketones are known, including those of propionylacetone, dibutylmethane, benzoylacetone, and furoylacetone.<sup>62,63</sup> Currently these compounds have limited analytical applications. Highly colored complexes of disalicylal ethylenediamine and its derivatives are known and may have value in analytical work.<sup>70</sup>

Uranium(IV) cupferrate, insoluble in water, is soluble in ether and other organic solvents and is an important complex in the chemistry of the uranium(IV) ion.