# COPPER COMPOUNDS

## 1. Introduction

Copper compounds, which represent only a small percentage of all copper production, play key roles in both industry and the biosphere. Copper [7440-50-8], mol wt = 63.546, $[\mathrm{Ar}]3d^{10}4s^1$, is a member of the first transition series and much of its chemistry is associated with the copper(II) ion [15158-11-9], $[\mathrm{Ar}]3d^9$. Copper forms compounds of commercial interest in the +1 and +2 oxidation states. The standard reduction potentials, $E^0$, for the reasonably attainable valence states of copper are

$$\mathrm{Cu}^+ + e^- \longrightarrow \mathrm{Cu}^o E^0 = 0.52\ \mathrm{V}$$

$$\mathrm{Cu}^{2+} + 2e^- \longrightarrow \mathrm{Cu}^o E^0 = 0.34\ \mathrm{V}$$

$$\mathrm{Cu}^{2+} + e^- \longrightarrow \mathrm{Cu}^+ E^0 = 0.15\ \mathrm{V}$$

$$\mathrm{Cu}^{3+} + e^- \longrightarrow \mathrm{Cu}^{2+} E^0 = 1.80\ \mathrm{V}$$

The copper(I) ion [17493-86-6] disproportionates spontaneously, $\mathrm{p}K = -5.95$, in aqueous solution according to

$$2\ \mathrm{Cu}^+ \longrightarrow \mathrm{Cu}^o + \mathrm{Cu}^{2+} \Delta E^0 = +0.37\ \mathrm{V}$$

The concentration of copper(I) ion remaining in solution is not appreciable. However, aqueous copper(I) ion can be stabilized by complex formation with various agents such as chloride, ammonia, cyanide, or acetonitrile.

The tri- or tetraamine complex of copper(I), prepared by reduction of the copper(II) tetraamine complex with copper metal, is quite stable in the absence of air. If the solution is acidified with a noncomplexing acid, the formation of copper metal, and copper(II) ion, is immediate. If hydrochloric acid is used for the neutralization of the ammonia, the insoluble cuprous chloride [7758-89-6], CuCl, is precipitated initially, followed by formation of the soluble ions $[\mathrm{CuCl_3}]^{2-}$, $[\mathrm{CuCl_4}]^{3-}$, and $[\mathrm{CuCl_5}]^{4-}$ as acid is increased in the system.

The copper(I) ion, electronic structure $[\mathrm{Ar}]3d^{10}$, is diamagnetic and colorless. Certain compounds such as cuprous oxide [1317-39-1] or cuprous sulfide [22205-45-4] are intensely colored, however, because of metal-to-ligand charge-transfer bands. Copper(I) is isoelectronic with zinc(II) and has similar stereochemistry. The preferred configuration is tetrahedral. Linear and trigonal planar structures are not uncommon, in part because the stereochemistry about the metal is determined by steric as well as electronic requirements of the ligands (see COORDINATION COMPOUNDS).

The stereochemical preference of the copper(II) ion is square planar or distorted octahedral because of the ligand field stabilization that arises from the $3d^9$ electronic configuration. This perturbation in an octahedral symmetry is known as Jahn-Teller distortion. Other configurations that occur for copper(II) include distorted tetrahedrons as well as a variety of five coordinate structures. Most copper(II) compounds are blue or green in color and exhibit a variety of magnetic phenomena (1). The majority of copper(II) compounds exhibit paramagnetic behavior as a result of the single unpaired 3*d* electron. There are, however, a significant number of polynuclear copper compounds that are sufficiently condensed to show spin–spin coupling of the unpaired electrons. This spin pairing may be so weak as to be observed only at near absolute zero temperatures or it may be strong enough to render the compound diamagnetic at room temperature or above. There have been reports of ferromagnetic polynuclear compounds as well. Probably the most significant, has been the high temperature superconductivity of copper oxide-containing materials (2,3).

## 2. Properties and Manufacture of Commercially Important Compounds

**2.1. Copper(II) Carbonate Hydroxide.** Basic copper carbonate, also named copper(II) carbonate hydroxide [12069-69-1], occurs in nature as the green monoclinic mineral malachite. The approximate stoichiometry is $CuCO_3 \cdot Cu(OH)_2$. There are two grades available commercially, the light and the dense. The light grade is produced by adding a copper salt solution to a concentrated solution of sodium carbonate, usually at 45–65°C. The blue, voluminous azurite [12070-39-2], $C_2H_2Cu_3O_8$, forms initially and converts to the green malachite within two hours. The dense product can be produced by boiling an ammoniacal solution to copper(II) carbonate (4) or by addition of a copper salt solution to sodium bicarbonate at 45–65°C. A dense product can also be produced by simultaneous addition of copper(II) salt solutions and soda ash solutions at controlled pH. Pure $CuCO_3$ has not been isolated.

Basic copper carbonate is essentially insoluble in water, but dissolves in aqueous ammonia or alkali metal cyanide solutions. It dissolves readily in mineral acids and warm acetic acid to form the corresponding salt solution.

**2.2. Copper Chloride.** Copper(I) chloride, CuCl, is a colorless or gray cubic crystal and occurs in nature as the mineral nantokite [14708-85-1]. The commercial product is white to gray to brown to green and of variable purity. Copper(I) chloride is usually produced at 450–900°C by direct combination of copper metal and chloride gas to yield a molten product (5–8). Once the reaction is initiated by heat it is self-sustaining and must be cooled. The molten product is variously cast, prilled, flaked, or ground depending on final use. Copper(I) chloride can be produced hydrometallurgically by reduction of copper(II) in the presence of chloride (9):

$$2\ CuCl_2 + \text{reducing agent} \longrightarrow 2\ CuCl + 2\ HCl + \text{oxidation product}$$

where the reducing agent can be sulfite, metallic copper, phosphorus acid, hydroxylamine, or zinc (10).

Copper(I) chloride is insoluble to slightly soluble in water. Solubility values between 0.001 and 0.1 g/L have been reported. Hot water hydrolyzes the material to copper(I) oxide. CuCl is insoluble in dilute sulfuric and nitric acids, but forms solutions of complex compounds with hydrochloric acid, ammonia, and alkali halide. Copper(I) chloride is fairly stable in air at relative humidities of less than 50%, but quickly decomposes in the presence of air and moisture.

Cupric chloride or copper(II) chloride [7447-39-4], $CuCl_2$, is usually prepared by dehydration of the dihydrate at 120°C. The anhydrous product is a deliquescent, monoclinic yellow crystal that forms the blue-green orthohombic, bipyramidal dihydrate in moist air. Both products are available commercially. The dihydrate can be prepared by reaction of copper carbonate, hydroxide, or oxide and hydrochloric acid followed by crystallization. The commercial preparation uses a tower packed with copper. An aqueous solution of copper(II) chloride is circulated through the tower and chlorine gas is sparged into the bottom of the tower to effect oxidation of the copper metal. Hydrochloric acid or hydrogen chloride is used to prevent hydrolysis of the copper(II) (11,12). Copper(II) chloride is very soluble in water and soluble in methanol, ethanol, and acetone.

Copper(II) oxychloride [1332-65-6], $Cu_2Cl(OH)_3$, is found in nature as the green hexagonal paratacamite [12186-00-4] or rhombic atacamite [1306-85-0]. It is usually precipitated by air oxidation of a concentrated sodium chloride solution of copper(I) chloride (13–15). Often the solution is circulated through a packed tower of copper metal, heated to 60–90°C, and aerated.

$$CuCl_2 + Cu \longrightarrow 2\ CuCl$$

$$6\ CuCl + 3\ H_2O + 3/2\ O_2 \longrightarrow CuCl_2 \cdot 3\ Cu(OH)_2 + 2\ CuCl_2$$

The mother liquor is separated from the product and returned to the tower. Copper(II) oxychloride is insoluble in water, but dissolves readily in mineral acids or warm acetic acid. The product dissolves in ammonia and alkali cyanide solution upon the formation of coordination complexes.

**2.3. Copper(II) Fluorides.** Copper(II) forms several stable fluorides, eg, cupric fluoride [7789-19-7], $CuF_2$, copper(II) fluoride dihydrate [13454-88-1], $CuF_2{\cdot}2H_2O$, and copper hydroxyfluoride [13867-72-6], CuOHF, all of which are interconvertible. When $CuF_2$ is exposed to moisture, it readily forms the dihydrate, and when the latter is heated in the absence of HF, $CuOHF \cdot H_2O$ results. The colorless crystals of anhydrous $CuF_2$ are triclinic in structure and are moisture sensitive, turning blue when exposed to moist air. Physical properties of $CuF_2$ are listed in Table 1. $CuF_2$ reacts with ammonia to form $CuF_2 \cdot 5NH_3$.

Several methods of synthesis for anhydrous $CuF_2$ have been reported, the most convenient and economical of which is the reaction of copper carbonate and anhydrous hydrogen fluoride to form the monohydrate, $CuF_2{\cdot}H_2O$. Part of the water content from the monohydrate is removed by addition of excess HF. The excess HF is decanted and the remaining mass transferred to a Teflon-lined tray and dried under an atmosphere of hydrogen fluoride. The decanted material may also be dehydrated in a nickel or copper tray under an atmosphere of fluorine at 150–300°C. Both routes have successfully resulted in ultrapure (99.95%) white $CuF_2$ in good yields. The other method for the preparation of high purity anhydrous copper(II) fluoride is by the direct fluorination of commercially available CuOHF (16), or the action of a mixture of HF and $BF_3$ on $CuF_2 \cdot 2H_2O$ (17).

**2.4. Copper Hydroxide.** Copper(II) hydroxide [20427-59-2], $Cu(OH)_2$, produced by reaction of a copper salt solution and sodium hydroxide, is a blue,

Table 1. **Physical Properties of $CuF_2$**

| Property | Value |
|---|---|
| molecular weight | 101.54 |
| melting point, °C | 785 ± 10 |
| boiling point, °C | 1676 |
| solubility, g/100 g | |
| water | 4.75 |
| anhydrous HF | 0.01 |
| aqueous 21.2% HF | 12.1 |
| density, $g/cm^3$ | 4.85 |
| $\Delta H_f$, kJ/mol[a] | −539 |
| $\Delta G_f$, kJ/mol[a] | −492 |
| $S$, J/(mol · K)[a] | 77.45 |
| $C_p$, J/(mol · K)[a] | 65.55 |

[a] To convert from J to cal, divide by 4.184.

gelatinous, voluminous precipitate of limited stability. The thermodynamically unstable copper hydroxide can be kinetically stabilized by a suitable production method. Usually ammonia or phosphates are incorporated into the hydroxide to produce a color-stable product. The ammonia processed copper hydroxide (18–21) is almost stoichiometric and copper content as high as 64% is not uncommon. The phosphate produced material (22,23) is lower in copper (57–59%) and has a finer particle size and higher surface area than the ammonia processed hydroxide. Other methods of production generally rely on the formation of an insoluble copper precursor prior to the formation of the hydroxide (24–28).

Copper hydroxide is almost insoluble in water (3 μg/L) but readily dissolves in mineral acids and ammonia forming salt solutions or copper ammine complexes. The hydroxide is somewhat amphoteric dissolving in excess sodium hydroxide solution to form trihydroxycuprate [37830-77-6], $[Cu(OH)_3]^-$, and tetrahydroxycuprate [17949-75-6], $[Cu(OH)_4]^-$.

**2.5. Copper Nitrates.** The trihydrate [10031-43-3] crystallizes as blue rhombic plates. Copper(II) nitrate hexahydrate [13478-38-1], $Cu(NO_3)_2 \cdot 6H_2O$, is produced by crystallization from solutions below the transition point of 26.4°C. A basic copper nitrate [12158-75-7], $Cu_2(NO_3)(OH)_3$, rather than the anhydrous product is produced on dehydration of the hydrated salts. The most common commercial forms for copper nitrate are the trihydrate and solutions containing about 14% copper. Copper nitrate can be prepared by dissolution of the carbonate, hydroxide, or oxides in nitric acid. Nitric acid vigorously attacks copper metal to give the nitrate and evolution of nitrogen oxides.

$$Cu + 4\ HNO_3 \longrightarrow Cu(NO_3)_2 + 2\ H_2O + 2\ NO_2$$

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$

The first reaction is favored at high temperatures and in the presence of concentrated acid.

The trihydrate is very soluble in water and ethanol. Decomposition begins around 80°C upon formation of the basic salt. At temperatures of 180°C the oxide is produced.

**2.6. Copper Oxides.** Copper(I) oxide [1317-39-1] is a cubic or octahedral naturally occurring mineral known as cuprite [1308-76-5]. It is red or reddish brown in color. Commercially prepared copper(I) oxides vary in color from yellow to orange to red to purple as particle size increases. Usually copper(I) oxide is prepared by pyrometallurgical methods. It is prepared by heating copper powder in air above 1030°C or by blending copper(II) oxide with carbon and heating to 750°C in an inert atmosphere. A particularly air-stable copper(I) oxide is produced when a stoichiometric blend of copper(II) oxide and copper powder are heated to 800–900°C in the absence of oxygen. Lower temperatures can be used if ammonia is added to the gas stream (29–31).

Various hydrometallurgical processes can be used to prepare copper(I) oxide. Acidification with sulfuric acid of ammonia complexes of copper(I) precipitates a red product. Vacuum distillation (32) of $Cu_2(NH_3)_4CO_3$ produces a stable red copper(I) oxide. Addition of sodium hydroxide to the same carbonate initially gives a yellow material which, on heating, turns orange. A boiling slurry of basic copper sulfate and copper sulfate solution can be reduced using sulfur dioxide to give a red product (33). Solutions of sodium copper(I) chloride can be neutralized using sodium hydroxide to give products of various colors depending on conditions (Table 2). Electrolytic processes can produce copper(I) oxide using copper electrodes in brine. Yellow material is produced at room temperature; orange and red products are made as the temperature is increased.

Copper(I) oxide is stable in dry air, but reacts with oxygen to form copper(II) oxide in moist air. $Cu_2O$ is insoluble in water, but dissolves in ammonia or hydrochloric acid. The product disproportionates to copper metal and copper(II) in dilute sulfuric or nitric acid.

Copper(II) oxide [1317-38-0], CuO, is found in nature as the black triclinic tenorite [1317-92-6] or the cubic or tetrahedral paramelaconite [71276-37-4]. Commercially available copper(II) oxide is generally black and dense although a brown material of low bulk density can be prepared by decomposition of the carbonate or hydroxide at around 300°C, or by the hydrolysis of hot copper salt solutions with sodium hydroxide. The black product of commerce is most often prepared by evaporation of $Cu(NH_3)_4CO_3$ solutions (37) or by precipitation of copper(II) oxide from hot ammonia solutions by addition of sodium hydroxide. An extremely fine (10–20 nm) copper(II) oxide has been prepared for use as a precursor in superconductors (38).

Table 2. **Copper(I) Oxides from the Reaction $2\ NaCuCl_2 + NaOH \longrightarrow Cu_2O + H_2O + 4\ NaCl$**

| | | Product | | |
|---|---|---|---|---|
| pH | Temperature, °C | Color | Particle size, μm | Reference |
| 7.0 | | yellow | 0.4 | 34 |
| 8.5 | 60 | orange | 1 | 35 |
| alkaline | 138 | red | 2.5 | 36 |
| 10.0[a] | 55 | purple | 48 | 34 |

[a] Reactants added simultaneously.

Copper(II) oxide is less often prepared by pyrometallurgical means. Copper metal heated in air to 800°C produces the copper(II) oxide. Decomposition of nitrates, carbonates, and hydroxides at various temperatures also occurs.

Copper(II) oxide is insoluble in water, but readily dissolves in mineral acid or in hot formic or acetic acids. CuO slowly dissolves in ammonia solution, but alkaline ammonium carbonate solubilizes it quickly.

**2.7. Copper(II) Sulfates.** Copper(II) sulfate pentahydrate [7758-99-8], $CuSO_4 \cdot 5H_2O$, occurs in nature as the blue triclinic crystalline mineral chalcanthite [13817-21-5]. It is the most common commercial compound of copper. The pentahydrate slowly effloresces in low humidity or above 30.6°C. Above 88°C dehydration occurs rapidly.

$$CuSO_4 \cdot 5\,H_2O \xrightarrow{88^\circ C} CuSO_4 \cdot 3\,H_2O \xrightarrow{114^\circ C} CuSO_4 \cdot H_2O$$

$$\xrightarrow{245^\circ C} CuSO_4 \xrightarrow{340^\circ C} 3\,Cu(OH)_2 \cdot CuSO_4 \xrightarrow{600^\circ C} CuO$$

The solubility and solution density as a function of temperature and acid concentration are given in Figure 1 (39). Crystallization of the pentahydrate can be effected both by concentrated and cooling or by addition of sulfuric acid. The former method is usually preferred because the crystals are of better structural integrity and thus more resistant to hard cake formation. Copper(II) sulfate can be prepared by dissolution of oxides, carbonates, or hydroxides in sulfuric acid solutions. Whereas copper metal does not displace hydrogen from acidic solution, aeration or oxygenation of hot dilute aqueous sulfuric acid in the presence of copper metal is a commonly used commercial method for $CuSO_4$ preparation (40). Solvent extraction is used to produce the pentahydrate from a variety of copper-containing liquors (4,39).

Copper(II) sulfate monohydrate [10257-54-2], $CuSO_4 \cdot H_2O$, which is almost white in color, is hygroscopic and packaging must contain moisture barriers. This product is produced by dehydration of the pentahydrate at 120–150°C.

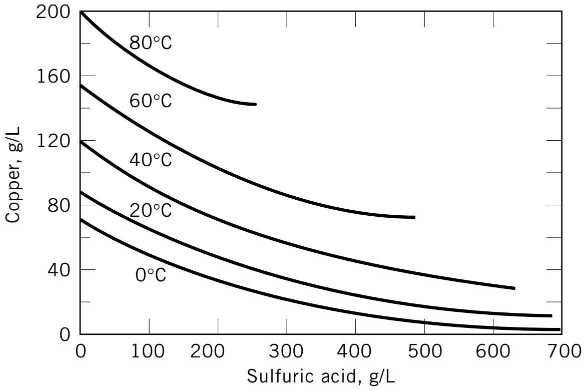

**Fig. 1.** Aqueous solubility of copper in copper sulfate as a function of sulfuric acid concentration at various temperatures. Reprinted with permission (39).

Trituration of stoichiometric quantities of copper(II) oxide and sulfuric acid can be used to prepare a material of limited purity. The advantages of the monohydrate as opposed to the pentahydrate are lowered freight cost and quickness of solubilization. However, these advantages are offset by the dustiness of the product and probably less than one percent of copper sulfate is used in the monohydrate form.

Anhydrous copper(II) sulfate [7758-98-7] is a gray to white rhombic crystal and occurs in nature as the mineral hydrocyanite. $CuSO_4$ is hygroscopic. It is produced by careful dehydration of the pentahydrate at 250°C. An impure product can also be produced from copper metal and hot sulfuric acid:

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\ H_2O$$

There are four basic sulfates that can be identified by potentiometric titration using sodium carbonate (41,42): langite [1318-78-1], $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$; brochantite [12068-81-4], $CuSO_4 \cdot 3Cu(OH)_2$; anterlite [12019-54-4], $CuSO_4 \cdot 2Cu(OH)_2$; and $CuSO_4 \cdot CuO \cdot 2Cu(OH)_2 \cdot xH_2O$. The basic copper(II) sulfate that is available commercially is known as the tribasic copper sulfate [12068-81-4], $CuSO_4 \cdot 3Cu(OH)_2$, which occurs as the green monoclinic mineral brochantite. This material is essentially insoluble in water, but dissolves readily in cold dilute mineral acids, warm acetic acid, and ammonia solutions.

Tribasic coppersulfate is usually prepared by reaction of sodium carbonate and copper sulfate. As the temperature of the reaction contents increases so does the size of the resulting particle. For use as a crop fungicide, intermediate (40–60°C) temperatures are used to obtain a fine particle. When lower temperatures are used to precipitate basic copper(II) sulfate, products high in sulfate and water of hydration are obtained.

## 3. Economic Aspects

Copper sulfate is the most important compound of copper. It is the starting material for the production of many other copper salts. However, 75% of production is used in agriculture, principally as a fungicide.

Today there are more than 100 manufacturers and the world's consumption is $200 \times 10^3$ t/yr (43).

Table 3 gives data on U.S. production of copper sulfate. Table 4 give U.S. export data and Table 5 gives U.S. import data for copper sulfate (44).

## 4. Analytical Methods

The specifications or typical analyses of selected copper compounds are given in Table 6 (45,46).

**4.1. Separation.** Preliminary separation of copper from a variety of interfering elements by extraction using diethyldithiocarbamate or dithizone has been practiced since the early 1940s (47–53) and is still commonly used (54,55). Excellent separations from a complex matrix can be effected using 2-hydroxyoximes (56), and precipitation of copper as the sulfide is commonplace.

Table 3. **U.S. Salient Copper Sulfate Statistics, t**[a,b]

| Copper sulfate | 1997 | 1998 | 1999 | 2000 | 2001 |
|---|---|---|---|---|---|
| production | 48,400 | 44,000 | 52,700 | 55,500 | 55,200 |
| exports | | | | | |
| refined | 92,900 | 86,200 | 25,200 | 93,600 | 22,500 |
| unmanufactured[c] | 628,000 | 412,000 | 395,000 | 650,000 | 556,000 |
| imports | | | | | |
| refined | 632,000 | 683,000 | 837,000 | 1,060,000 | 991,000 |
| unmanufactured[c] | 999,000 | 1,190,000 | 1,280,000 | 1,350,000 | 1,400,000 |

[a] From Ref. 44.

[b] Data are rounded to no more than three significant digits.

[c] Includes copper content of alloy scrap.

Hydrolysis to give basic salts of copper is quite often used, using collectors such as lanthanum (57) or iron(III) (58,59). Numerous ammonia-insoluble impurities in copper can be separated by coprecipitation with lanthanum using ammonia (60). Selective precipitation with trithiocarbonate ion (61), or concentration

Table 4. **U.S. Exports of Copper Sulfate by Country**[a,b]

| Country | Quantity, t | Value, $\times 10^3$ $ |
|---|---|---|
| 2000 | 10,300 | 25,100 |
| 2001: | | |
| Australia | 276 | 656 |
| Brazil | 49 | 134 |
| Canada | 843 | 1,620 |
| Chile | 302 | 620 |
| China | 693 | 1,510 |
| Denmark | 348 | 773 |
| France | 95 | 263 |
| Germany | 24 | 118 |
| Hong Kong | 226 | 420 |
| India | 1 | 3 |
| Indonesia | 392 | 828 |
| Italy | 197 | 480 |
| Japan | 992 | 2,370 |
| Korea, Republic of | 2,070 | 4,550 |
| Mexico | 110 | 246 |
| Netherlands | 116 | 253 |
| New Zealand | 169 | 392 |
| Saudi Arabia | 20 | 46 |
| Singapore | 559 | 1,300 |
| Sweden | 1,420 | 3,380 |
| Taiwan | 599 | 1,400 |
| United Kingdom | 1,250 | 3,110 |
| Venezuela | 8 | 22 |
| other | 239 | 600 |
| *Total* | *11,000* | *25,100* |

[a] From Ref. 44.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

Source: U.S. Census Bureau.

Table 5. **U.S. Imports for Consumption of Copper Sulfate by Country**[a,b]

| Country | Quantity, t | Value, $\times 10^3$ \$[c] |
|---|---|---|
| 2000 | 2,550 | 9,910 |
| 2001: | | |
| Australia | 2,150 | 4,020 |
| France | 69 | 188 |
| Germany | 99 | 359 |
| Hong Kong | 195 | 220 |
| Japan | 5 | 70 |
| Mexico | 2,090 | 3,720 |
| United Kingdom | 6 | 43 |
| other | 35 | 68 |
| *Total* | *4,650* | *8,680* |

[a] From Ref. 44.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

[c] C.i.f. value at U.S. port.

Source: U.S. Census Bureau.

using ammonium pyrrolidine dithiocarbamate [5108-96-3] (APDC) or dithiooxamide (62) can be used. Ion exchange (qv) using Chelex 100 has been used to preconcentrate trace copper (63–66) Chelating ion exchangers have been developed for selective preconcentration (67) or are used in hydrometallurgical applications (68) (see CHELATING AGENTS; METALLURGY; TRACE AND RESIDUE ANALYSIS).

**4.2. Determination.** The most accurate (69) method for the determination of copper in its compounds is by electrogravimetry from a sulfuric and nitric acid solution (46). Pure copper compounds can be readily titrated using ethylene diamine tetracetic acid (EDTA) to a SNAZOXS or Murexide endpoint. Iodometric titration using sodium thiosulfate to a starch–iodide endpoint is one of the most common methods used industrially. This latter titration is quicker than electrolysis, almost as accurate, and much more tolerant of impurities than is the titration with EDTA. Gravimetry as the thiocyanate has also been used (69).

Table 6. **Analyses of Copper Compounds**

| | Composition, wt% | | | | |
|---|---|---|---|---|---|
| Assay | $Cu(OH)_2CuCO_3$ | $Cu(NO_3)_2 \cdot 3\ H_2O$ | CuO | $CuSO_4 \cdot 5\ H_2O$ | $CuSO_4 \cdot 5\ H_2O$ |
| grade | light | solution | black | technical | electronic |
| Cu | 55.4 | 14.0 | 78.5 | 25.3 | 25.5 |
| Fe | 0.1 | 0.002 | 0.01 | 0.01 | 0.003 |
| Pb | 0.005 | 0.002 | 0.01 | 0.005 | 0.001 |
| Zn | 0.015 | 0.0005 | 0.05 | 0.01 | 0.0005 |
| insolubles | 0.05[a] | | 0.02[a] | 0.05[b] | 0.008[b] |
| ABD[c], $kg/m^3$ | 300 | 1450 | 1300 | 1000 | 1000 |

[a] Insoluble in $HNO_3$.

[b] Insoluble in $H_2O$.

[c] Apparent or free-falling bulk density.

Colorimetric procedures are often used to determine copper in trace amounts. Extraction of copper using diethyldithiocarbamate can be quite selective (61,63), but the method using dithizone is preferred because of its greater sensitivity and selectivity (51–53). Atomic absorption spectroscopy, atomic emission spectroscopy, x-ray fluorescence, and polargraphy are specific and sensitive methods for the determination of trace level copper.

## 5. Health and Safety Factors

Copper is one of the twenty-seven elements known to be essential to humans (70–73) (see MINERAL NUTRIENTS). The daily recommended requirement for humans is 2.5–5.0 mg (74). Copper is probably second only to iron as an oxidation catalyst and oxygen carrier in humans (75). It is present in many proteins, such as hemocyanin [9013-32-3], galactose oxidase [9028-79-9], ceruloplasmin [9031-37-2], dopamine β-hydroxylase, monoamine oxidase [9001-66-5], superoxide dismutase [9054-89-1], and phenolase (76,77). Copper aids in photosynthesis and other oxidative processes in plants.

Copper is toxic in exceedingly low concentrations to most fungi, algae, and certain bacteria and can be lethal to higher life forms in relatively high doses. The $LD_{50}$'s in mg/kg for rats are copper(II) acetate, 710; copper(II) chloride dihydrate, 163; anhydrous copper(II) nitrate, 940; and copper(II) sulfate pentahydrate, 300. For female rats, copper hydroxide has an $LD_{50}$ of 2200 mg/kg. The acute oral toxicity in humans, $LD_{LO}$, is 100 mg/kg, but recovery from ingestion of 600 mg/kg has occurred. The symptoms of copper poisoning are nausea, vomiting, cramps, gastric disturbances, apathy, anemia, convulsions, coma, and death. Chronic toxicity from copper poisoning has not been definitely observed although there are numerous accounts of chronic poisoning resulting from the refining of copper. This poisoning is now thought to be a result of the common impurities in copper ores such as lead, selenium, and arsenic (78,79). Copper is known to accumulate in the liver, but it is uncertain whether pathological changes occur.

Inhalation of dusts can cause metal fume fever (80,81), and ulceration or perforation of the nasal septum. Mild discomfort has been noted with workplace concentrations as low as 0.08 $mg/m^3$. The workplace standard ACGIH (TLV) for copper dusts or mist is 1 $mg/m^3$ and 0.2 $mg/m^3$ for copper fume (82). OSHA PEL TWA for dust, mist is 1 $mg/m^3$ and for fumes and respirable particles is 0.1 $mg/m^3$ (83).

## 6. Uses

Examples of uses (43,84) of copper compounds are given in Table 7 which lists the materials of primary industrial importance. The majority of copper compounds are used as fungicides, nutritionals, and algicides.

**6.1. Foliar Fungicides and Bactericides.** Of the ~70,000 t/yr as copper in compounds used in agriculture, almost 75% is used in the control of fungi (see FUNGICIDES, AGRICULTURAL). The first reference to the use of copper as a fungicide dates to 1761 (95) where copper sulfate was used on wheat seed for the control of bunt. In 1807 (96) the discovery of copper as a fungicide was made

Table 7. **Uses of Copper Compounds**

| Compound | CAS Registry number | Molecular formula | Uses |
|---|---|---|---|
| copper(I) acetate | [598-54-9] | $CuCH_3COO$ | absorption of olefins |
| copper(II) acetate | [142-71-2] | $Cu(CH_3COO)_2$ | fabrics, textiles, pigment, catalyst, paper treatment |
| copper(II) acetate monohydrate | [6046-93-1] | $Cu(CH_3COO)_2 \cdot H_2O$ | |
| copper(II) acetate, basic | [52503-63-6] | $Cu(CH_3COO)_2 \cdot CuO \cdot 6H_2O$ | manufacture of Paris Green fungicides, pigments, textiles |
| copper(II) arsenate | [7778-41-8] | $Cu_3(AsO_4) \cdot 4H_2O$ | insecticides, wood preserving, antifouling pigment |
| copper(I) bromide | [7787-70-4] | $CuBr$ | catalyst |
| copper(II) bromide | [7789-45-9] | $CuBr_2$ | catalyst, brominating reagent, intensifier (photography) |
| copper(II) carbonate, basic | [12069-69-1] | $CuCO_3 \cdot Cu(OH)_2$ | fungicides, animal feeds, catalyst, oil treatment |
| copper(I) chloride | [7758-89-6] | $CuCl$ | catalyst, absorption of CO, fuel oil treatment |
| copper(II) chloride | [7447-39-4] | $CuCl_2$ | catalyst, mordant, electroplating, pigment |
| copper(II) chloride dihydrate | [10125-13-0] | $CuCl_2 \cdot 2H_2O$ | |
| copper(II) chloride hydroxide | [1332-65-6] | $CuCl_2 \cdot 3Cu(OH)_2$ | fungicides, pigment |
| copper(II) chromate(VI) | [13548-42-0] | $CuCrO_4$ | wood preserving, textiles |
| copper(II) chromate(III) | [12018-10-9] | $CuCr_2O_4$ | hydrogenation catalyst |
| copper(I) cyanide | [544-92-3] | $CuCN$ | electroplating, catalyst |
| copper(II) fluoride | [7789-19-7] | $CuF_2$ | fluorinating agent, superconductors, cathode material, isomerization, herbicide, termite repellant, catalyst[a] |
| copper(II) formate | [544-19-4] | $Cu(HCO)_2$ | mildewcide, bactericide |
| copper(II) fluoborate | [38465-60-0] | $Cu(BF_4)_2$ | electroplating, electronics |
| copper(II) gluconate | [527-09-3] | $Cu(C_6H_{11}O_7)_2$ | dietary supplement, breath freshener |
| copper(II) hydroxide | [20427-59-2] | $Cu(OH)_2$ | fungicides, rayon manufacture, catalyst, antifouling pigment, electrolysis, electroplating |
| copper(I) iodide | [7681-65-4] | $CuI$ | heat and light stabilizer in polymers, photographic emulsions, and light-sensitive paper, and in oil drilling to aid in corrosion inhibition in highly acid environments; used as feed additive, in cloud seeding, and as a double salt with mercury(II) iodide as a temperature indicator |

Table 7 *(Continued)*

| Compound | CAS Registry number | Molecular formula | Uses |
|---|---|---|---|
| copper(II) naphthenate | [1338-02-9] | | fungicide, mildewcide in textiles, woods, and paints |
| copper(II) nitrate | [3251-23-8] | $Cu(NO_3)_2$ | electrolysis and electroplating, electronics, fuel oil treatment, colorant, pyrotechnics, catalyst |
| Copper(II) nitrate trihydrate | [10031-43-3] | $Cu(NO_3)_2 \cdot 3H_2O$ | |
| copper(II) oleate | [1120-44-1] | $C_{18}H_{34}O_2 \cdot 1/2Cu$ | fuel oil combustion improver, emulsifier, dispersant, antifouling coating for fish nets and lines |
| copper(II) oxalate | [814-91-5] | $CuC_2O_4$ | catalyst, stabilizer |
| copper(I) oxide | [1317-39-1] | $Cu_2O$ | antifouling pigment, fungicide, pigment, catalyst, seed dressings |
| copper(II) oxide | [1317-38-0] | $CuO$ | wood preserving, feed additive, pigment, catalyst, mineral supplements |
| copper(II) phosphate trihydrate | [7798-23-4] | $Cu_3(PO_4)_2 \cdot 3H_2O$ | fungicide, corrosion inhibitor |
| copper(II) diphosphate hydrate | [10102-90-6] | $Cu_2P_2O_7 \cdot xH_2O$ | electroplating plastics, aluminum, and zinc |
| copper(II) stearate | [660-60-6] | $C_{18}H_{36}O_2 \cdot 1/2Cu$ | antifouling paints, wood and textile preservation |
| copper(II) sulfate | [7758-98-7] | $CuSO_4$ | fungicides, algicides, antifouling paints, electrolysis and electroplating, electronics, fuel oil treatment, wood preserving |
| copper(II) sulfate pentahydrate | [7758-99-8] | $CuSO_4 \cdot 5H_2O$ | |
| copper(II) sulfate, tribasic | [12068-81-4] | $CuSO_4 \cdot 3Cu(OH)_2$ | fungicides |
| copper(I) sulfide | [22205-45-4] | $Cu_2S$ | luminous paints, solar cells, semiconductors, lubricants |
| copper(II) sulfide | [1317-40-4] | $CuS$ | antifouling pigment, manufacture of aniline black |
| copper(I) thiocyanate | [1111-67-7] | $CuSCN$ | antifouling pigment |

[a] From Refs. 85–94.

and the discovery of Bourdeaux mixture (copper sulfate plus lime) followed in 1882.

In order for copper to have any persistance as a foliar fungicide it must be rendered insoluble so that it is not washed off the leaf surface during rainfall. Copper compounds have been used successfully since the latter 1880s on fruit, vegetables, nut crops, and ornamentals. Copper is an effective broad-spectrum fungicide, although its action is more prophylactic in nature.

Whereas copper is not as effective as some organics against specific pathogens, pathogen resistance to copper has been minimal in the >100 year usage. Many organic fungicides are used less often then copper compounds because of residue tolerance, grower reluctance, or for regulatory reasons. Use of copper compounds as fungicides has seen a resurgence in the latter part of the twentieth century.

**6.2. Plant and Animal Nutrient.** Copper is one of seven micronutrients that has been identified as essential to the proper growth of plants (97). Cereal crops are by far the most affected by copper deficiency (see WHEAT AND OTHER CEREAL GRAINS). Greenhouse studies have shown yield increases from 38% to over 500% for wheat, barley, and oats (98) using copper supplementation. A tenfold increase in the yield of oats was reported in France (99). Symptoms of copper deficiency vary depending on species, but often it is accompanied by withering or chlorosis in the leaves that is not ammenable to iron supplementation. In high concentrations, particularly in low pH soils, copper can be toxic to plants.

Copper compounds are used as feed additives in Europe and the United States primarily for chickens and swine (see FEEDS AND FEED ADDITIVES) (100,101). Copper increases the rate of gain and feed efficiencies of the animals. It is unclear whether this results from overcoming animal deficiencies or by enhancing preservation of feedstuffs.

**6.3. Algicides.** Copper sulfate has been used to control algae in lakes and reservoirs since around 1905. In the United States it is used by every state either on a routine or an occasional basis (102). It provides an effective and ecologically sound method to control algal blooms. Algae cause water supplies to have odor and taste. The turbidity and scum that forms from algal blooms can blind filters and affect certain industries adversely. Significant algal blooms decrease recreational use and are a primary cause of oxygen depletion that results in fish kills.

Copper sulfate is by far the most common algicide. Other copper-containing algicides for use in domestic applications such as swimming pools are usually chelated to prevent hydrolysis and precipitation of the copper.

**6.4. Other Uses.** Copper is one of the primary ingredients used in wood preservation. In combination with chromium and arsenic or zinc or borates it has largely replaced pentachlorophenol and creosote. As an antifouling pigment, copper(I) oxide has found renewed use because of regulatory problems of organotin compounds (see COATINGS, MARINE). Copper is much more amenable to the environment than the tin or lead alternatives. Copper phthalocyanines are excellent color-stable blue and green pigments for paints (see PHTHALOCYANINE COMPOUNDS). As an oxidation catalyst, copper with chrome is used extensively. Mixed oxides of chromium and copper show promise as a replacement for platinum group metals in emission control devices. Copper used with zinc or with zinc and chromium is employed as a low temperature shift catalyst (LTS) for the synthesis of fuels and methanol from coal gases (see COAL CONVERSION PROCESSES; FUELS, SYNTHETIC). Electroplating uses copper sulfate baths extensively and electroless copper baths are used to produce circuit boards (see ELECTROLESS PLATING). Copper oxide is used in air-bag technology, and oxides and sulfides are used as solar collectors (see SOLAR ENERGY). Copper compounds are also used as fuel additives to minimize sulfide and carbon monoxide emissions.

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