SILVER COMPOUNDS

1. Introduction

Silver, a white, lustrous metal, slightly less malleable and ductile than gold (see GOLD AND GOLD COMPOUNDS), has high thermal and electrical conductivity (see SILVER AND SILVER ALLOYS). Most silver compounds are made from silver nitrate [7761-88-8], $AgNO_3$, which is prepared from silver metal.

Some silver metal is found in Nature, frequently alloyed with other metals such as copper, lead, or gold. Naturally occurring silver compounds, however, are the primary sources of silver in the environment. The most abundant naturally occurring silver compound is silver sulfide [21548-73-2] (argentite), Ag_2S, found alone and combined with iron, copper, and lead sulfides. Other naturally occurring silver compounds are silver sulfonantimonite [15983-65-0] (pyrargyrite), Ag_3SbS_3, silver arsenite [15122-57-3] (proustite), Ag_3AsS_3, silver selenide [1302-09-6], and silver telluride [12653-91-7]. Silver chloride (chlorargyrite) and silver iodide (iodargyrite) have also been found in substantial quantities in the western United States.

Silver is a soft metal that preferentially forms lower oxidation states (+1, +2) and binds preferentially with sulfur (1). Studies show that silver levels in uncontaminated fine-grain sediments are typically similar to those for average crustal abundance, 0.05 μg/g concentration of silver in fresh lake and river waters is typically <0.2 μg/L, while those in contaminated estuary and harbor waters may be upward of from 5.1 to 33.9 μg/g (2) produces a linear co-ordination of connecting bonds (3). It has one of the highest electronegativities resulting in strong covalent bonds. Its oxides are weakly held and are dissociate at about 200°C. Silver is significantly more permeable to oxygen than are other materials and has found use as a filter for the production of pure atomic oxygen (4). Silver binds extremely strongly to $S(11^-)$ ligands compared to all other ligands (5). Silver is rapidly adsorbed onto particles present in natural waters, and its concentration after a discharge is quickly reduced to background or upstream levels through dilution and sedimentation (qv) (6–8).

Silver belongs to Group 11 (IB) of the Periodic Table. The metal has a $4d^{10}5s^1$ outer electronic configuration. Silver has been shown to have three possible positive oxidation states, but only silver(I) is stable in aqueous solution. The silver(II) ion, a powerful oxidizing agent, is a transient species in solution. The two silver(II) compounds that have been studied are the oxide and the fluoride. Silver(III) exists only when stabilized through complex formation.

Silver compounds, available from commercial suppliers, are expensive. Reagent grades of silver(I) carbonate, cyanide, diethyldithiocarbamate, iodate, nitrate, oxide, phosphate, and sulfate are available. Standardized solutions of silver nitrate are also available for analytical uses. Purified grades of silver(I) acetate, bromide, cyanide, and iodide can be purchased; silver nitrate is also made as a USP XX grade for medicinal uses (3).

All silver compounds are bactericidal. Release of a silver ion from a silver compound results in destruction of bacteria it contacts (9). Commercial biocides use many compounds that supply the silver ion, such as silver chloride, silver citrate, polyvalent silver oxide, and silver zeolite. On the other hand, the action of silver thiosulfate in cut flowers is to block the production of ethylene that causes wilting, it has become the backbone of the cut flower industry in the United States.

Many silver compounds are unstable to light, and are thus are shipped and stored in brown glass or opaque plastic bottles. Silver compounds that are oxidants, eg, silver nitrate and iodate, must be so identified according to U.S. Department of Transportation (DOT) regulations. Compounds such as silver cyanide, which is toxic owing to its cyanide content, must carry a poison label. However, most silver compounds are essentially nontoxic to mammals.

2. Silver(I) Compounds

The solubility and solubility product constants, K_{sp}, for many silver compounds are given in Table 1 (4,5,10).

2.1. Silver Acetate. Silver acetate [563-63-3], $H_3CCOOAg$, is prepared from aqueous silver nitrate and acetate ion. Colorless silver acetate crystals and solutions made from this salt are unstable to light.

2.2. Silver Azide. Silver azide, AgN_3, is prepared by treating an aqueous solution of silver nitrate with hydrazine (qv) or hydrazoic acid. It is shock-sensitive and decomposes violently when heated.

2.3. Silver Acetylide. Silver acetylide [7659-31-6] (silver carbide), Ag_2C_2, is prepared by bubbling acetylene through an ammoniacal solution of silver nitrate. Silver acetylide is sensitive to the point of undergoing detonation on contact.

2.4. Silver Bromate. Silver bromate [7783-89-3], $AgBrO_3$, a readily dissolved silver salt for studies of silver ion chemistry.

2.5. Silver Bromide. Silver bromide [7785-89-3], AgBr, is formed by the addition of bromide ions to an aqueous solution of silver nitrate. The light yellow to green-yellow precipitate is less soluble in ammonia than silver chloride, but it easily dissolves in the presence of other complexing agents, such as thiosulfate ions.

Silver bromide crystals, formed from stoichiometric amounts of silver nitrate and potassium bromide, are characterized by a cubic structure having interionic distances of 0.29 nm. If, however, an excess of either ion is present, octahedral crystals tend to form. The yellow color of silver bromide has been attributed to ionic deformation, an indication of its partially covalent character. Silver bromide melts at 434°C and dissociates when heated $>500°C$.

Silver bromide is significantly more photosensitive than silver chloride, resulting in the extensive use of silver bromide in photographic products. The crystal structure of photographic silver bromide is often octahedral.

2.6. Silver Carbonate. Silver carbonate [534-16-7], Ag_2CO_3, is produced by the addition of an alkaline carbonate solution to a concentrated solution of silver nitrate. The pH and temperature of the reaction must be carefully controlled to prevent the formation of silver oxide. A suspension of Ag_2CO_3 is slightly basic because of the extensive hydrolysis of the ions present. Heating solid Ag_2CO_3 to 218°C gives Ag_2O and CO_2.

2.7. Silver Chloride. Silver chloride [7783-90-6], AgCl, is a white precipitate that forms when chloride ion is added to a silver nitrate solution. The order of solubility of the three silver halides is $Cl^- > Br^- > I^-$. Because of the formation of complexes, silver chloride is soluble in solutions containing excess chloride and in solutions of cyanide, thiosulfate, and ammonia. Silver chloride is insoluble in nitric and dilute sulfuric acid. Treatment with concentrated sulfuric acid gives silver sulfate.

Silver chloride crystals are face-centered cubic (fcc), having a distance of 0.28 nm between each ion in the lattice. Silver chloride, the most ionic of the halides, melts at 455°C and boils at 1550°C. Silver chloride is very ductile and can be rolled into large sheets. Individual crystals weighing up to 22 kg have been prepared (11).

The silver ion in silver chloride can be readily reduced by light, and is used to a great extent in photographic print papers. Sufficient light intensity and time leads to silver chloride decomposing completely into silver and chlorine.

2.8. Silver Chromate. Silver chromate [7784-01-2], Ag_2CrO_4, is prepared by treating silver nitrate with a solution of chromate salt or by heating a suspension of silver dichromate [7784-02-3].

2.9. Silver Cyanide. Silver cyanide [506-64-9], AgCN, forms as a precipitate when stoichiometric quantities of silver nitrate and a soluble cyanide are mixed. Silver(I) ion readily forms soluble complexes, ie, $Ag(CN)^-{}_2$ or $Ag(CN)^{2-}{}_3$, in the presence of excess cyanide ion.

2.10. Silver Cyclohexanebutyrate. Silver cyclohexanebutyrate [62638-04-4], $Ag[COO(CH_2)_3C_6H_{11}]$ provides silver for studies of silver in non-ionic hydrocarbons and oils.

2.11. Silver Fluoride. Silver fluoride [7783-95-1], AgF, is prepared by treating a basic silver salt such as silver oxide or silver carbonate, with hydrogen fluoride. Silver fluoride can exist as the anhydrous salt, a dihydrate [72214-21-2] (<42°C), and a tetrahydrate [22424-42-6] (<18°C). The anhydrous salt is colorless, but the dihydrate and tetrahydrate are yellow. Ultraviolet light or electrolysis decomposes silver fluoride to silver subfluoride [1302-01-8], Ag_2F, and fluorine.

2.12. Other Silver Halogen-Containing Salts. All silver halides are reduced to silver by treating an aqueous suspension with more active metals, such as magnesium, zinc, aluminum, copper, iron, or lead. Alternatively, the dry salts are reduced by heating with turnings or powders of these metals. Photolyzed silver halides are also reduced by organic reducing agents or developers, eg, hydroquinone, *p*-aminophenol, and *p*-phenylenediamine, during photographic processing (see PHOTOGRAPHY).

Halates. Silver chlorate, $AgClO_3$, silver bromate, $AgBrO_3$, and silver iodate, $AgIO_3$, have been prepared. The halates may decompose explosively if heated.

2.13. Silver Iodide. Silver iodide, AgI, precipitates as a yellow solid when iodide ion is added to a solution of silver nitrate. It dissolves in the presence of excess iodide ion, forming an AgI_2 complex; however, silver iodide is only slightly soluble in ammonia and dissolves slowly in thiosulfate and cyanide solutions.

Silver iodide exists in one of three crystal structures depending on the temperature, a phenomenon frequently referred to as trimorphism. Below 137°C, silver iodide is in the cold cubic, or γ-form; at 137–145.8°C, it exists in the green-yellow colored hexagonal, or β-form; >145.8°C, the yellow cubic or α-form of silver iodide is the stable crystal structure. Silver iodide decomposes into its elements at 552°C.

Although silver iodide is the least photosensitive of the three halides, it has the broadest wavelength sensitivity in the visible spectrum. This feature makes silver iodide particularly useful in the photographic industry. It resists reduction by metals, but is reduced quantitatively by zinc and iron in the presence of sulfuric acid.

2.14. Silver Lactate. Silver lactate [128-00-7], $CH_3CH(OH)CO_2AG$, a human-safe compound and soluble in alcoholic or aqueous media for studies of anti-infective personal products.

2.15. Silver Molybdenum Oxide. Silver molybdenum oxide [13765-74-7], Ag_2MoO_4, for studies of silver as a stabilizer of crystal structures such as those of molybdenum, and also studies of catalytic properties.

2.16. Silver Nitrate. Silver nitrate [7761-88-8], $AgNO_3$, is the most important commercial silver salt because it serves as the starting material for all other silver compounds. It is prepared by the oxidation of silver metal with hot nitric acid. The by-products are nitrogen oxides, NO and NO_2, which are vented to the atmosphere or scrubbed out of the fumes with an alkaline solution. Heavy metal impurities, such as copper, lead, and iron, are precipitated by increasing the pH of the solution to 5.5–6.5 with silver oxide and then boiling. The solution containing silver nitrate is made slightly acid, heated, evaporated, and then poured into pans to cool and crystallize. The crystals are washed, centrifuged, and dried. They can be further purified by recrystallization from hot water.

The Kestner-Johnson dissolver is widely used for the preparation of silver nitrate (12). In this process, silver bars are dissolved in 45% nitric acid in a pure oxygen atmosphere. Any nitric oxide, NO, produced is oxidized to nitrogen dioxide, NO_2, which in turn reacts with water to form more nitric acid and nitric oxide. The nitric acid is then passed over a bed of granulated silver in the presence of oxygen. Most of the acid reacts. The resulting solution contains silver at ~840 g/L (13). This solution can be further purified using charcoal (14), alumina (15), and ultraviolet (uv) radiation (16).

The manufacture of silver nitrate for the preparation of photographic emulsions requires silver of very high purity. At the Eastman Kodak Company, the principal U.S. producer of silver nitrate, 99.95% pure silver bars are dissolved in 67% nitric acid in three tanks connected in parallel. Excess nitric acid is removed from the resulting solution, which contains 60–65% silver nitrate, and the solution is filtered. This solution is evaporated until its silver nitrate concentration is 84%. It is then cooled to prepare the first crop of crystals. The mother liquor is purified by the addition of silver oxide and returned to the initial stages of the process. The crude silver nitrate is centrifuged and recrystallized from hot, demineralized water. Equipment used in this process is made of ANSI 310 stainless steel (17).

Silver nitrate forms colorless, rhombic crystals. It is dimorphic and changes to the hexagonal rhombohedral form at 159.8°C. It melts at 212°C to a yellowish liquid which solidifies to a white, crystalline mass on cooling. An alchemical name, lunar caustic, is still applied to this fused salt. In the presence of a trace of nitric acid, silver nitrate is stable to 350°C. It decomposes at 440°C to metallic silver, nitrogen, and nitrogen oxides. Solutions of silver nitrate are usually acidic, having a pH of 3.6–4.6. Silver nitrate is soluble in ethanol and acetone.

In the absence of organic matter, silver nitrate is not photosensitive. It is easily reduced to silver metal by glucose, tartaric acid, formaldehyde, hydrazine, and sodium borohydride.

2.17. Silver Nitrite. Silver nitrite [7783-99-5], $AgNO_2$, is prepared from silver nitrate and a soluble nitrite, or silver sulfate and barium nitrite.

2.18. Organic Acid Salts. Slightly soluble or insoluble silver salts are precipitated when mono- and dicarboxylic aliphatic acids or their anions are treated with silver nitrate solutions. Silver behenate [2489-05-6], $C_{22}H_{43}O_3Ag$; silver laurate [18268-45-6], $C_{12}H_{23}O_2Ag$; and silver stearate [3507-99-1], $C_{18}H_{35}O_2Ag$, are used in commercial applications. Silver oxalate [533-51-7], $C_2O_4Ag_2$, decomposes explosively when heated.

2.19. Silver Oxide. Silver oxide [20667-12-3], Ag_2O, a dark brown to black material, is formed when an excess of hydroxide ion is added to a silver nitrate solution. Silver oxide can also be prepared by heating finely divided silver metal in the presence of oxygen. Anhydrous silver oxide is difficult to prepare. Reagent-grade material may contain up to 1 wt% water. Silver oxide is soluble in most silver-complexing agents. However, if a suspension of silver oxide in excess hydroxide is treated with ammonium hydroxide, highly explosive fulminating silver, or Bertholet's silver (18), may be produced.

When heated to 100°C, silver oxide decomposes into its elements. Thermodynamically, silver is metallic over 200°C, oxides are unstable over that temperature, however, there is always some oxygen in the silver lattice. Silver oxide and sulfur form silver sulfide. Silver oxide absorbs carbon dioxide from the air, forming silver carbonate. (Sec. 4, Other Oxidation States).

2.20. Silver Permanganate. Silver permanganate [7783-98-4], $AgMnO_4$, is a violet solid formed when a potassium permanganate solution is added to a silver nitrate solution. It decomposes upon heating, exposure to light, or by reaction with alcohol.

2.21. Perhalates. Whereas silver perchlorate [7783-93-9], $AgClO_4$, and silver periodate [15606-77-6], $AgIO_4$, are well known, silver perbromate [54494-97-2], $AgBrO_4$, has more recently been described (19). Silver perchlorate is prepared from silver oxide and perchloric acid, or by treating silver sulfate with barium perchlorate. Silver perchlorate is one of the few silver salts that is appreciably soluble in organic solvents such as glycerol, toluene, and chlorobenzene.

2.22. Silver Phosphates. Silver phosphate [7784-09-0], or silver orthophosphate, Ag_3PO_4, is a bright yellow material formed by treating silver nitrate with a soluble phosphate salt or phosphoric acid. Silver pyrophosphate [13465-97-9], $Ag_4P_2O_7$, is a white salt prepared by the addition of a soluble pyrophosphate to silver nitrate. Both the phosphate and the pyrophosphate are light sensitive. Silver pyrophosphate turns red upon exposure to light.

2.23. Silver Selenate. Silver selenate, Ag_2SeO_4, is prepared from silver carbonate and sodium selenate (see SELENIUM AND SELENIUM COMPOUNDS).

2.24. Silver Sulfate. Silver sulfate [10294-26-5], $Ag_8S_2O_4$, is prepared by treating metallic silver with hot sulfuric acid. Alternatively, a solution of silver nitrate is acidified with sulfuric acid and the nitric acid is evaporated, leaving a solution of silver sulfate. Silver sulfate is more soluble in sulfuric acid than in water because of the formation of silver hydrogen sulfate [19287-89-9], $AgHSO_4$.

Silver sulfate decomposes above 1085°C into silver, sulfur dioxide, and oxygen. This property is utilized in the separation of silver from sulfide ores by direct oxidation. Silver sulfate is reduced to silver metal by hydrogen, carbon, carbon monoxide, zinc, and copper.

2.25. Silver Sulfide. Silver sulfide [21548-73-2], Ag_2S, forms as a finely divided black precipitate when solutions or suspensions of most silver salts are treated with an alkaline sulfide solution or hydrogen sulfide. Silver sulfide has a dimorphic crystal structure. Transition from the rhombic (acanthite) to the cubic (argentite) form occurs at 175°C. Both crystal structures are found in nature.

Silver sulfide is one of the most insoluble salts known. It is not solubilized by nonoxidizing mineral acids, but it is soluble in concentrated nitric acid, concentrated sulfuric acid, and alkaline cyanide solutions.

Silver and sulfur combine even in the cold to form silver sulfide. The tendency of silver to tarnish is an example of the ease with which silver and sulfur compounds react. Polishes that contain silver complexing agents, such as chloride ion or thiourea, are used to remove silver tarnish.

Silver sulfide is exceptionally stable in air and sunlight, but decomposes when heated to 810°C. Moss silver (filiform silver), consisting of long hair-like growths of pure silver, is formed when silver sulfide is heated for a prolonged period at elevated temperatures $<810°C$.

2.26. Silver Sulfite. Silver sulfite, Ag_2SO_3, is obtained as a white precipitate when sulfur dioxide is bubbled through a solution of silver nitrate. Silver sulfite is unstable to light and heat, and solutions decompose when boiled.

2.27. Silver Tetrafluoroborate. Silver tetrafluoroborate [14104-20-2], $AgBF_4$, is formed from silver borate and sodium borofluoride or bromine trifluoride. It is soluble in organic solvents.

2.28. Silver Thiocyanate. Silver thiocyanate [1701-93-5], AgSCN, is formed by the reaction of stoichiometric amounts of silver ion and a soluble thiocyanate.

2.29. Silver Thiosulfate. Silver thiosulfate [23149-52-2], $Ag_2S_2O_3$, is an insoluble precipitate formed when a soluble thiosulfate reacts with an excess of silver nitrate. In order to minimize the formation of silver sulfide, the silver ion can be complexed by halides before the addition of the thiosulfate solution. In the presence of excess thiosulfate, the very soluble $Ag_2(S_2O_3)^{4-}{}_3$ and $Ag_2(S_2O_3)^{6-}{}_5$ complexes form. These soluble thiosulfate complexes, which are very stable, are the basis of photographic fixers. Silver thiosulfate complexes are oxidized to form silver sulfide, sulfate, and elemental sulfur (see THIOSULFATES).

3. Silver(I) Complexes

Silver is a class B soft metal that preferentially forms complexes with sulfur^{2-} containing ligands. Silver can be expected to bind most strongly to S-containing and I-containing ligands and more weakly to N-containing and O-containing ligands (20). Linear polynuclear complexes are known. The usual species are AgL and AgL_2, but silver complexes up to AgL_4 have been identified. Many of these complexes have commercial application.

3.1. Ammonia and Amine Complexes. In the presence of excess ammonia (qv), silver ion forms the complex ions $Ag(NH_3)^+{}_2$ and $Ag(NH_3)^+{}_3$. To minimize the formation of fulminating silver, these complexes should not be prepared from strongly basic suspensions of silver oxide. Highly explosive fulminating silver, believed to consist of either silver nitride or silver imide, may detonate spontaneously when silver oxide is heated with ammonia or when alkaline solutions of a silver–amine complex are stored. Addition of appropriate amounts of HCl to a solution of fulminating silver renders it harmless. Stable silver complexes are also formed from many aliphatic and aromatic amines, eg, ethylamine, aniline, and pyridine.

3.2. Cyanide Complexes. Insoluble silver cyanide [506-64-9], AgCN, is readily dissolved in an excess of alkali cyanide. The predominant silver species present in such solutions is $Ag(CN)^-{}_2$, with some $Ag(CN)^{2-}{}_3$ and $Ag(CN)^{3-}{}_4$. Virtually all silver salts, including the insoluble silver sulfide, dissolve in the presence of excess cyanide because the dissociation constant for the $Ag(CN)^-{}_2$ complex is only 4×10^{-19} (see CYANIDES).

3.3. Halide Complexes. Silver halides form soluble complex ions, AgX_2^- and AgX_3^{2-}, with excess chloride, bromide, and iodide. The relative stability of these complexes is $I^- > Br^- > Cl^-$. Complex formation affects solubility greatly. The solubility of silver chloride in 1 *N* HCl is 100 times greater than in pure water.

3.4. Olefin Complexes. Silver ion forms complexes with olefins and many aromatic compounds. As a general rule, the stability of olefin complexes decreases as alkyl groups are substituted for the hydrogen bonded to the ethylene carbon atoms (21).

3.5. Sulfur Complexes. Silver compounds other than sulfide dissolve in excess thiosulfate. Stable silver complexes are also formed with thiourea. Except for the cyanide complexes, these sulfur complexes of silver are the most stable. In photography, solutions of sodium or ammonium thiosulfate fixers are used to solubilize silver halides present in processed photographic emulsions. When insoluble silver thiosulfate is dissolved in excess thiosulfate, various silver complexes form. At low thiosulfate concentrations, the principal silver species is $Ag_2(S_2O_3)^{2-}{}_2$; at high thiosulfate concentrations, species such as $Ag_2(S_2O_3)^{10-}{}_6$ are present. Silver sulfide dissolves in alkaline sulfide solutions to form complex ions such as $Ag(S_4)^{3-}{}_2$ and $Ag(HS)^{2-}{}_4$. These ions are found in hot springs and waters highly charged with H_2S (22). Silver forms stable, slightly ionized salts with aliphatic and aromatic thiols.

3.6. Organic Complexes. The sulfadiazine salt of silver has been shown to posses significantly more bactericidal action than sulfadiazine alone, and has become the most widely used antibacterial in the treatment of burn wounds (23). Other organic complexes have been studied including, silver quinolones (24) with similar antibacterial action.

4. Other Oxidation States

4.1. Silver(II) Compounds. Silver(II) is stabilized by coordination with nitrogen heterocyclic bases, such as pyridine and dipyridyl. These cationic complexes are prepared by the peroxysulfate oxidation of silver(I) solutions in the presence of an excess of the ligand. An extensive review of the higher oxidation states of silver has been published (25).

Silver Difluoride. Silver(II) fluoride [7783-95-1], AgF_2, is a brown to black hygroscopic material obtained by the treatment of silver chloride with fluorine gas at 200°C (26) or by the action of fluorine gas on silver metal. It is a strong oxidizing agent and a strong fluorinating agent. When heated $>450°C$, it decomposes into AgF and fluorine. It also decomposes in aqueous solutions unless stabilized with concentrated HNO_3.

Silver(II) Oxide. Silver(II) oxide [1301-96-8], [35366-11-1], AgO, is prepared by persulfate oxidation of Ag_2O in basic medium at 90°C or by the anodic oxidation of solutions of silver(I) salts. It is stable to 100°C, dissolves in acids, and evolves oxygen and gives some Ag^{2+} in solution.

Silver(II) oxide is a strong oxidant. Reactions in alkaline medium have been studied extensively (19). It decomposes in aqueous solution unless stabilized with concentrated nitric acid.

4.2. Silver(III) Compounds. Only one simple compound exists with silver(III) ions. It is made by the addition of oxidizing agents such as sodium peroxydisulfate to silver nitrate and sodium hydroxide. The result is a black diamagnetic oxide with a unit cell of ($2Ag^+$ $2Ag^{3+}$ $4O^{2-}$) [155645-89-9] (27,28): $4AgNO_3 + 2Na_2S_2O_8 + 8NaOH = Ag_4O_4 + 4Na_2SO_4 + 4NaNO_3 + 4H_2O$. When mixtures of potassium or cesium halides are heated with silver halides in a stream of fluorine gas, yellow $KAgF_4$ [23739-18-6] or $CsAgF_4$ [53585-89-0], respectively, are obtained. These compounds are diamagnetic and extremely sensitive to moisture (25). When Ag_2SO_4 is treated with aqueous potassium persulfate in the presence of ethylenedibiguanidinium sulfate, the relatively stable Ag(III)−ethylenebiguanide complex is formed.

5. Economic Aspects

The cost of silver compounds is related to the silver bullion market price. The annual average U.S. price for silver per troy ounce (the international standard weight for pricing precious metals in markets worldwide) was $4.832/tr oz during 1990, and $4.37/tr oz during the year 2001.

In the year 2001, the estimated consumption of silver for fabrication in United States, including the use of scrap, was ~5300 metric tons (169 million tr oz), and for the world 27,400 metric tons (880 million tr oz) (29). Approximately three quarters of mined silver was as a by-product of lead/zinc, copper, and gold mines. The world total of mined silver amounted to ~18,320 metric tons (90 million tr oz) in 2001. The normal shortfall between mine production and fabrication demand is made up by silver obtained from recycled jewelry and coins, discarded photographic film and spent photographic solutions, and scrapped electrical/electronics products. A comprehensive review of the world silver market is published yearly (29).

Year	High	Low	Average
1985	216	179	197
1986	199	157	176
1987	328	172	225
1988	257	193	210

6. Analytical Methods

6.1. Qualitative. The classic method for the qualitative determination of silver in solution is precipitation as silver chloride with dilute nitric acid and chloride ion. The silver chloride can be differentiated from lead or mercurous chlorides, which also may precipitate, by the fact that lead chloride is soluble in hot water but not in ammonium hydroxide, whereas mercurous chloride turns black in ammonium hydroxide. Silver chloride dissolves in ammonium hydroxide because of the formation of soluble silver–ammonia complexes. A number of selective spot tests (30) include reactions with *p*-dimethylamino-benzlidenerhodanine, ceric ammonium nitrate, or bromopyrogallol red [16574-43-9]. Silver is detected by X-ray fluorescence and arc-emission spectrometry. The silver electrode is capable of measuring white silver to 1 mg/L in clean freshwater, but not natural water, or effluents from publically owned treatment tanks. The silver electrode will work in natural seawater at these concentrations (31). Measuring silver in the mg/L range using the inductively coupled plasma-mass spectrometer is possible, but requires special techniques in addition to ultra-clean techniques.

6.2. Quantitative. Classically, silver concentration in solution has been determined by titration with a standard solution of thiocyanate. Ferric ion is the indicator. The deep red ferric thiocyanate color appears only when the silver is completely titrated. Gravimetrically, silver is determined by precipitation with chloride, sulfide, or 1,2,3-benzotriazole. Silver can be precipitated as the metal by electrodeposition or chemical reducing agents. A colored silver diethyldithiocarbamate complex, extractable by organic solvents, is used for the spectrophotometric determination of silver complexes.

Highly sensitive instrumental techniques, such as X-ray fluorescence, atomic absorption spectrometry, and inductively coupled plasma optical emission spectrometry, have wide application for the analysis of silver in a multitude of materials. In order to minimize the effects of various matrices in which silver may exist, samples are treated with perchloric or nitric acid. Direct-aspiration atomic absorption (32) and inductively coupled plasma (33) have silver detection limits of 10 and 7 μg/L, respectively. The use of a graphic furnace in an atomic absorption spectrograph lowers the silver detection limit to 0.2 μg/L.

Instrumental methods are useful for the determination of the total silver in a sample, but such methods do not differentiate the various species of silver that may be present. A silver ion-selective electrode measures the activity of the silver ions present in a solution. These activity values can be related to the concentration of the free silver ion in the solution. Commercially available silver ion-selective electrodes measure Ag^+ down to 10 μg/L, and special silver ion electrodes can measure free silver ion at 1 ng/L (34) (see ELECTROANALYTICAL TECHNIQUES).

7. Health and Safety Factors

7.1. The Silver Ion. It is the silver ion (Ag^+) that provides silver with its unique recognition as the healthful metal. Its bactericidal activity is unique because though this ion breeches walls of bacterial cells, it does not do so to mammalian cells. This selectivity, which remains unclear, was perceived during ancient times leading to its universal use.

A study with a transmission electron microscope (TEM) and an x-ray microanalysis instrument revealed the action of silver against two classes of bacteria: gram-negative *Escherichia coli* (*E. coli* ATCC 23282) and gram-positive *Staphylococcus aureus* (*S. aureus*, ATCC 35696). The TEM photograph of untreated *E. coli* is shown in Fig. 1 and treated in Fig. 2, revealed serious damage to the *E. coli* cell walls and marked changes to the interior (35). Microanalysis of the interior revealed a significant amount of silver in combination with sulfur-containing cell components. The TEM photographs of *S. aureus*, showed similar though smaller effects suggesting that action *S. aureus* may have a stronger defense system against silver ions. In the lighter shade interior, a large amount of phosphorous was detected. The authors proposed that this was a condensed form of DNA molecules where phosphorous is a primary component.

Studies conducted at the Laboratory of Cellular & Molecular Biology, National Institute on Aging, NIH, in determining how metal ions interact with nucleic acid structures, revealed that Ag^+ replaces the H-bonds preferentially in the GC regions of the DNA double helix resulting helix having a much larger diameter. Subjected to hydrolysis, the larger diameter Ag-treated helix was virtually unhydrolyzed after 30 hours reaction time indicating that the silver ion stabilizes the polynucleotide structure in such a way that cleavage becomes far more difficult (36). A second effect is the consolidation of the DNA molecules into highly compacted 3-dimensional structures, reducing viability (37).

The first state regulation requiring the clinical use of a silver compound, was the administration a 1% to 2% silver nitrate [7761-88-8] solution to the eyes of newborns. It was the consequence of observations by the German obstetrician, C.S.F. Crede, who observed a relationship of children committed to institutions of the blind and their exposure to maternal venereal disease (38). The introduction in 1884 of Crede's prophylaxis became a state regulation in every civilized country in the world.

As silver nitrate is far too aggressive an agent for general clinical use. Argyrol a silver salt of the protein vitellin, was introduced in 1902 as a mild general antiseptic for topical infections by A. C. Barnes, a Philadelphia chemist. It satisfied a ready market until eclipsed by the biocides.

An investigator for the Office of Scientific Research and Development during WWII, C. L. Fox, M.D., observed that those with severe war wounds and burns commonly succumbed to bacterial infection. His investigations into the sulfonamide drugs as a topical antibacterial therapy led him to evaluate silver sulfadiazine [22199-08-2] (39). This drug delivered all the antibacterial advantages of the silver ion, but none of the disadvantages of silver nitrate, such as its ready reaction with chlorides on the surface of a wound essentially removing the silver ion from the action against the bacteria. Unlike silver nitrate, silver sulfadiazine [22199-08-2] is active against both gram positive and gram negative organisms, fungi, and protozoa, including mouse malaria. It is also topically effective against viruses such as herpes, and sexually transmitted diseases such as genital herpes, gonorrhea, trichomonas, and *treponema pallidia* (40).

R. O. Becker, M.D., Department of Orthopaedic Surgery, Health Science Center, State University of New York, Syracuse, NY, recognized that the antibiotic effectiveness of the silver ion could be limited to incidental contact with bacteria in the surrounding media. To force silver ions to flood a wound he developed a small electric circuit (~0.9 V) to drive silver ions through a wound (41). Over two decades of *in vivo* and *in vivo* studies with animals and humans showed that electrically driven silver accelerated tissue growth by five to six times faster than non-silver-treated tissue. Electric current alone is unsatisfactory, but the addition of silver as the positive anode to provide electrically driven silver ions to flood the wound, consistently significant accelleration of reconstruction results.

Becker's observed an unexpected rate of wound regeneration with the electrically-driven silver ions, "...the evident enhancement of healing is the direct result of the cellular changes..." (42). Clearly the silver ion was either promoting a reversion of committed mammalian cells to a more primitive mode (stem cells) more readily assimilated in restoration or the Ag^+ was stimulating the reproduction of already-present stem cells within the human system. Studies have indicated that primitive or stem cells are indeed present in muscle (43), in bone marrow (44), and in fibrous tissue (45).

Becker states, "The failure to other non-toxic metal ions to produce a similar alteration using the same electrical parameters strongly indicates that the electrically generated silver ion is the agent responsible for the observed cellular changes." He also observed that following electrically-driven silver ion treatment, "The subsequent resumption of normal morphology and activity indicates the lack of any lasting toxic effects from the silver ions" (44).

According to the Public Health Service Drinking Water Standards (Public Health Service, U.S. DHEW, 1962), the need to set a standard for silver (Ag) arose from its intentional addition to waters for disinfection. "It is reasonable to assume that vegetables belonging to the family Brassicaceae, such as cabbages, turnip, cauliflower, and onion, would combine with residual silver in the cooking water. The content of several liters of water could thus be ingested." A tentative drinking water standard for silver was set based upon a lifetime maximum of 1 gram of silver to produce argeria, as determined by the onset of argeria from the injection of 8 grams Ag-arsphenamine. Assuming that all the silver ingested is deposited in the skin, a limit of 50 μg/L could be ingested approximately 27 years without exceeding a silver deposition of 1 g.

In 1989, silver was dropped from EPA's 1962 Drinking Water Priority List (46), because "there is either little or no potential for exposure via drinking water, or no adverse health effect associated with [its] presence in drinking water. In 1991, EPA announced, "Three contaminants on the 1988 Drinking Water Priority List (DWPL)—ammonia, silver, and sodium—have been determined to be of low priority for regulation and therefore have been dropped from the 1991 list [and placed on the secondary contaminant list]. For each of these three substances, there is either little or no potential for exposure via drinking water, or no adverse health effect associated with their presence in drinking water" (47).

Further in 1991, Part 143 (40 CFR 143) on National Secondary Drinking Water Regulations, the table in Section 143.3 on Secondary maximum contaminant levels was revised to read as follows: "Contaminant: Silver, Level: 0.1 mg/L (48). This increase from the previous limit of 0.05 mg/L permitted an effective concentration of the silver ion for the sanitation of drinking water and swimming pool water. It also recognized that higher concentrations of the silver ion would be deleterious to aquatic organisms.

The quest for healthful, odor-free swimming pools began in the 1930s. The discovery that silver and copper ions generated by a mild electric current would adequately sanitize private swimming pools led to serious interest in silver sanitation. Following years of satisfactory sanitation of pools and hot tubs, a protocol for the certification of silver/copper ionization systems was developed by the National Sanitation Foundation/International, Ann Arbor, MI. For such systems, the CDC has suggested a chlorine residual of 0.2 ppm instead of the usual 3 ppm recommended when only chlorine is used. The exception is the approval of polyvalent silver oxide ($2\ Ag^{+1} + 2\ Ag^{+3} + 4\ O^{-2}$) [155645-89-9] for swimming pool sanitation without the need for chlorine (EPA No. 3432-64) (49,50).

Natural Defenses. All vertebrates, invertebrates, and microorganisms possess defenses against accumulation of the heavy metals. Metals not sequestered for the healthy function of the organism are removed by proteins known as metallothioneins. These transport, store, and detoxify essential and nonessential trace metals (51). Metallothioneins encapsulating heavy metals are excreted mostly by the liver in the feces. Supersaturation of this protective system may result in the excess metals binding with available thiols, binding the silver ions as silver sulfide (52–54).

Removal of silver deposits in the skin has proved not feasible. Argyria is a condition requiring long, acute exposure to silver fumes or sprays. Modern industrial practice, requiring face masks, gloves, and reactions under hoods avoids such exposure. There is no evidence that silver causes cancer (55).

Aquatic Organisms. Fish intake oxygen through gills which supply physiological input and output as diverse as those associated with the lungs and kidneys of mammals. In freshwater fish, sufficient concentrations of silver and/or copper inhibit the uptake of sodium through the gills. This disturbance of internal balance may lead to a decrease in the levels of sodium, chlorides, and other ions which in turn triggers the potential of cardiovascular collapse and death (56).

In 1989, the medical profession determined that the deposition of silver in internal organs and skin (argyria and argyrosis) did not impair the functions of the affected organs. Thus argyria and argyrosis are considered to be cosmetic effects, not adverse health effects. In response, the U.S. Environmental Protection Agency (EPA) removed silver from the list of maximum contaminant levels (MCL) regulated in drinking water in 1991 (57) and increased the recommended limit of silver in drinking water to 100 μg/L to protect against argeria (a coloration of the skin resulting from excessive ingestion of silver).

Silver compounds having anions that are inherently toxic, eg, silver arsenate and silver cyanide, can cause adverse health effects. The reported rat oral LD values for silver nitrate, silver arsenate [13510-44-6], and silver cyanide are 500–800 (58), 200–400 (58), and 123 mg/kg (59), respectively.

Effects from chronic exposure to soluble silver and silver compounds seem to be limited to deposition without evidence of health impairment (58,61,62). Argyria and argyrosis have resulted from therapeutic and occupational exposures to silver and its compounds. These disorders are characterized by either localized or general deposition of a silver–protein complex in parts of the body, and impart a blue-gray discoloration to the areas affected. In generalized argyria, characteristic discoloration may appear on the face, ears, forearms, and under the fingernails (62). Although the exact quantities of silver required for the development of argyria are not known, estimates based on therapeutic exposure suggest that the gradual accumulation of 1–5 g leads to generalized argyria (63). Localized argyria can occur as a result of the prolonged handling of metallic silver, which causes silver particles to be embedded in the skin and subcutaneous tissues via sweat-gland pores, or following the application of silver compounds to abraded skin areas (64). In argyrosis, silver is deposited primarily in the cornea and conjunctiva. This does not, however, appear to cause visual impairment (58,61).

Occupational argyria is unknown because of effective industrial hygiene practices. In 1980, the American Conference of Governmental Industrial Hygienists (ACGIH) adopted a TLV for airborne silver metal particles of 100 μg/m^3, and proposed a TLV of 10 μg/m^3, as silver, for airborne soluble silver compounds (65). These values were selected to protect against argyria and argyrosis from industrial exposures to silver and silver compounds. Argyria caused by the excessive therapeutic use of silver compounds is extremely rare because of the very small amount of silver required for effective treatment.

In 1980, the EPA published ambient water quality criteria for silver. An upper limit of 50 μg/L in natural waters was set to provide adequate protection against adverse health effects (66). In 1991, EPA revised the 1988 Drinking Water Priority List to delete ammonia, silver, and sodium from that list because, "... there is either little or no potential for exposure via drinking water, or no adverse health effect associated with their presence in drinking water" (47). In 1991 the EPA also increased the secondary maximum, contaminant levels for silver from 50 μg/L (50 ppb) to 100 μg/L (100 ppb) (48). In 1992, EPA deleted the human health criteria for silver from the ambient water quality criteria to be consistent with the drinking water standards (67).

8. Environmental Impact

The impact that a silver compound has in water is a function of the free or weakly complexed silver ion concentration generated by that compound, not the total silver concentration (6–8,34,68,69). In a standardized, acute aquatic bioassay, fathead minnows were exposed to various concentrations of silver compounds for a 96-h period and the concentration of total silver lethal to half of the exposed population (96-h LC_{50}) determined. For silver nitrate, the value obtained was 16 μg/L. For silver sulfide and silver thiosulfate complexes, the values were >240 and >280 mg/L, respectively, the highest concentrations tested (34).

The chronic aquatic effects which relate silver speciation to adverse environmental effects were studied on rainbow trout eggs and fry. The maximum acceptable toxicant concentration (MATC) for silver nitrate, as total silver, was reported to be 90–170 ng/L (70). Using fathead minnow eggs and fry, the MATC, as total silver, for silver thiosulfate complexes was reported as 21–44 mg/L, and for silver sulfide as 11 mg/L, the maximum concentration tested (34).

Free ionic silver readily forms soluble complexes or insoluble materials with dissolved and suspended material present in natural waters, such as sediments and sulfide ions (71). The hardness of water is sometimes used as an indicator of its complex-forming capacity. Although earlier studies suggested hardness of water reduces the toxicity of silver, many researchers have shown that not to be the case. Chloride, natural organic matter, and sulfide clusters have been shown to be the major ligands that reduce silver toxicity in natural fresh waters, and salinity in marine waters. Although the U.S. EPA still recommends use of the 1980 Ambient Water Quality Criteria for silver, they are aware that hardness has little effect in protecting aquatic organisms. The U.S. EPA is currently revising the Cu and Ag water quality control documents, using the major ligands to establish site-specific criteria (the Bureau of Land Management approach) (72).

In the manufacture of photographic materials, silver is originally present as a halide. When light-exposed photographic films and papers are processed, the silver halide that has not been affected by light is normally removed by solubilization as a thiosulfate complex using a thiosulfate-containing fixing bath. Before disposing of exhausted fixing baths, most of the silver is recovered, frequently by metallic exchange or by electrolytic reduction. The resulting concentrations of silver thiosulfate complex in the final effluents are 0.1–20 mg/L, as total silver (34). Silver being a precious metal is recovered from photoprocessing effluents to levels at or below 1 mg/L (see: the Silver Council webside, and the Code of Management Practice for photoprocessors procedures).

In secondary wastewater treatment plants receiving silver thiosulfate complexes, microorganisms convert this complex predominately to silver sulfide and some metallic silver (see WASTES, INDUSTRIAL). These silver species are substantially removed from the treatment plant effluent at the settling step (73,74). Any silver entering municipal secondary treatment plants tends to bind quickly to sulfide ions present in the system and precipitate into the treatment plant sludge (75). Thus, silver discharged to secondary wastewater treatment plants or into natural waters is not present as the free silver ion but rather as a complexed or insoluble species and is quickly bound to sulfide ions from almost any source (76). This means that negligible Ag exists as the "free ion," but is mostly bound to these sulfides in oxic as well as anoxic environments. Toxicologically, the silver bound to these sulfide ions or clusters is the strong suppression of the Ag effect on most sensitive organisms (77).

9. Uses

9.1. Analysis. The ability of silver ion to form sparingly soluble precipitates with many anions has been applied to their quantitative determination. Bromide, chloride, iodide, thiocyanate, and borate are determined by the titration of solutions containing these anions using standardized silver nitrate solutions in the presence of a suitable indicator. These titrations use fluorescein, tartrazine, rhodamine 6-G, and phenosafranine as indicators (78). Attention must be paid to the photo degradation of silver in the solution.

Silver diethyldithiocarbamate [1470-61-7] is a reagent commonly used for the spectrophotometric measurement of arsenic in aqueous samples (79) and for the analysis of antimony (80). Silver iodate is used in the determination of chloride in biological samples such as blood (81).

Combination silver–silver salt electrodes have been used in electrochemistry. The potential of the common Ag/AgCl (saturated)–KCl (saturated) reference electrode is +0.199 V. Silver phosphate is suitable for the preparation of a reference electrode for the measurement of aqueous phosphate solutions (82). The silver–silver sulfate–sodium sulfate reference electrode has also been described (83). The Ag_2S electrode is the most robust and stable of all the specific ion electrodes, if used properly. Being a low impedance electrode, it needs a high ionic medium and high flow (double junction) electrode. If the solution is well buffered, free ion concentration (activities) can be measured to 10^{-19} or less. Typical calibration in silver nitrate gives *dl* of $\sim 10^{-5.8}$ *M* (or 10 μg/L as stated). Like any other trace substance, ambient concentration-contaminant effects appear if the system is not well buffered for Ag^+. References on silver specific electrodes are as well as books on specific ion electrodes. The key problem is fouling of the surface, and as mentioned, high flow of ions in the electrode measuring system.

9.2. Batteries. Primary, ie, nonrechargeable, batteries containing silver compounds have gained in popularity through use in miniaturized electronic devices. The silver oxide–zinc cell has a cathode of Ag_2O or AgO. These cells are characterized by a high energy output per unit weight and a fairly constant voltage, ~1.5 V, during discharge. Originally used almost exclusively for military applications, satellites, and space probes, silver oxide–zinc batteries are used as of this writing (~2002) as power sources for wrist watches, pocket calculators, and hearing aids. Silver batteries have excellent shelf stability. Ninety percent of the original capacity is retained after one year of storage at 21°C (see BATTERIES, PRIMARY CELLS). Silver chromate is one of several oxidizing agents that can be used in lithium primary batteries (84). Calcium–silver technology was introduced for automobile battery grids in the mid-1990s. Silver provides additional strength to the lead grid giving it a 20% increase in service life despite increased operating temperatures and meets the increased power demand due to extensive electrical systems. The starting power is about the same, but power can be drawn from the battery more efficiently, especially at winter temperatures, providing better starting performance and better service life. The addition of silver markedly reduces the corrosion of the grid, the most important limiting factor in the life of the battery. Its use is becoming almost universal.

Silver sulfide, when pure, conducts electricity like a metal of high specific resistance, yet it has a zero temperature coefficient. This metallic conduction is believed to result from a few silver ions existing in the divalent state, and thus providing free electrons to transport current. The use of silver sulfide as a solid electrolyte in batteries has been described (85).

9.3. Catalysts. Silver does not hold oxygen very strongly. The oxygen molecule is efficiently dissociated on the surface of silver into atomic oxygen atoms that are weakly adsorbed on the surface of the silver. When a molecule such as ethylene, methanol, hydrocarbons, or bacteria, impacts the atomic oxygen-rich silver surface, it reacts readily with the weakly held atomic oxygen atoms. The reactant molecule does not react with the silver because the silver is almost inert, it rather reacts with the weakly held oxygen on the surface and consequently oxidation takes place—silver is a true catalyst (86).

Silver has been used for oxidation and dehydrogenation of single- and two-carbon organic compounds for >100 years. Marked improvement in the purity of product (selectivity) has been achieved when in combination with other elements such as chlorine or alloyed with elements such as gold or palladium. The actual catalytic process over silver has been elucidated in detail (86). A two-stage Ag–Cu catalyst system increased the production of formaldehyde from 90 to 94% any without decrease in formaldehyde selectivity (86).

Silver has, however, been unsatisfactory for oxidation of long-chain hydrocarbons because the bonds in multiple carbons are weaker and easily broken on meeting the atomic oxygen on the silver surface into carbon dioxide and water. This action has been offset by the addition of alkali metal salts such as CsCl to the silver to lower the desorption energy of an olefin epoxide, dramatically increasing the activity, selectivity, and catalyst lifetime of silver for the longer hydrocarbon chains. The catalytic preparation of epoxybutene and its derivatives represent the beginning of new families of chemicals now available for fine chemical production. More than 100 chemicals have been prepared with such additions so far (87).

A combined sorption–catalytic process converts the methanol and mercaptans in Kraft mill waste gas condensates into formaldehyde (86). Similarly, the solubility of silver tetrafluoroborate in organic solvents has enhanced its use in the synthesis of 3-pyrrolines by the cyclization of allenic amines (88).

Silver carbonate, alone or on Celite, has been used as a catalyst for the oxidation of methyl esters of D-fructose (89), ethylene (90), propylene (91), trioses (92), and α-diols (93). The mechanism of the catalysis of alcohol oxidation by silver carbonate on Celite has been studied (94).

Silver sulfate has been described as a catalyst for the reduction of aromatic hydrocarbons to cyclohexane derivatives (95). It is also a catalyst for oxidation reactions, and as such has long been recommended for the oxidation of organic materials during the determination of the COD of wastewater samples (96,97) (see WASTES, INDUSTRIAL; WATER, INDUSTRIAL WATER TREATMENT).

9.4. Cloud Seeding. In 1947, it was demonstrated that silver iodide could initiate ice crystal formation because, in the β-crystalline form, it is isomorphic with ice crystals. As a result, cloud seeding with silver iodide has been used in weather modifications attempts such as increases and decreases in precipitation (rain or snow) and the dissipation of fog. Optimum conditions for cloud seeding are present when precipitation is possible but the nuclei for the crystallization of water are lacking.

Silver iodide crystals, or smoke, for cloud seeding are produced predominantly by ground-based steady-state generators. Short-term (5–10-min) flares are also used. In one study, ground-based generators produced an average of 255-g silver iodide crystals per hour. Each generator is designed to cover a 259-km (100-mi) target area. Cloud seeding is reviewed in Reference 98. Studies of high alpine mountain lakes determined that there were no adverse environmental effects from cloud seeding operations (99).

9.5. Electroplating. Most silver-plating baths employ alkaline solutions of silver cyanide. The silver cyanide complexes that are obtained in a very low concentration of free silver ion in solution produce a much firmer deposit of silver during electroplating than solutions that contain higher concentrations. An excess of cyanide beyond that needed to form the $Ag(CN)_2^-$ complex is employed to control the Ag^+ concentration. The silver is added to the solution either directly as silver cyanide or by oxidation of a silver-rod electrode. Plating baths frequently contain 40–140 g/L of silver cyanide (100) (see ELECTROPLATING).

9.6. Mirrors. The use of silver for the production of mirrors results in a highly reflective coating (visible light-97% reflection; infrared-99%). The mirror is produced by the reaction of two separate solutions on the glass surface to be coated. One contains silver ammonia complex, the other an organic reducing agent, eg, formaldehyde, sodium potassium tartrate, sugar, or hydrazine. After rinsing, the silver coating can be protected by copper plating or silicone coating (101). The precipitation of silver on glass using sodium hydroxide is well known. A far safer method of silvering glass uses an amine reducer such as glucosaminic acid added to a silver nitrate and ammonium hydroxide solution to cause the deposition of silver onto the glass, improving both quality and adhesion (102).

9.7. Photography. The largest single use of silver and its compounds is in the photographic industry (103,104). Silver nitrate and a halide salt of an alkali metal or an ammonium halide give a light-sensitive silver halide. The silver halide can account for up to 30–40% of the total emulsion weight. Gelatin is the other primary constituent (see EMULSIONS; PHOTOGRAPHY). Many different silver halide emulsions are manufactured; the ratios of the halides and preparation details are adjusted according to the specific properties and applications desired. For photographic papers and the emulsions of low sensitivity, silver chloride, chlorobromide, or bromide is employed. Emulsions of high sensitivity are primarily bromide plus up to 10 mol % of silver iodide. Pure silver iodide emulsions are not commercially important and silver fluoride has no comparable photographic use.

Heat-processed photographic systems have been described that utilize silver behenate, silver laurate, and silver stearate. These silver salts are coated on paper in the presence of organic reducing agents (101,106).

Newer methods of image recording seek to avoid the high cost of silver. However, continued research has not led to systems that are able to offer the same combination of high sensitivity, high image density, exceptional resolution, permanence, and tricolor recording. In color photography (qv), dyes comprise the finished image, and the emulsion silver is removed during processing. Silver ions present in the photographic fixing solution as a silver thiosulfate complex can be recovered by metallic replacement, electroplating, or chemical precipitation.

9.8. Other Uses. Photochromic glass contains silver chloride (107) and silver molybdate [13765-74-7] (108) (see CHROMOGENIC MATERIALS). An apparatus coated with silver nitrate has been described for the detection of rain or snow (109). Treatment with silver–thiosulfate complex has been reported as dramatically increasing the postharvest life of cut carnations (110). Silver sulfate has been used in the electrolytic coloring of aluminum (111). Silver sulfate also imparts a yellowish-red color to glass bulbs (112).

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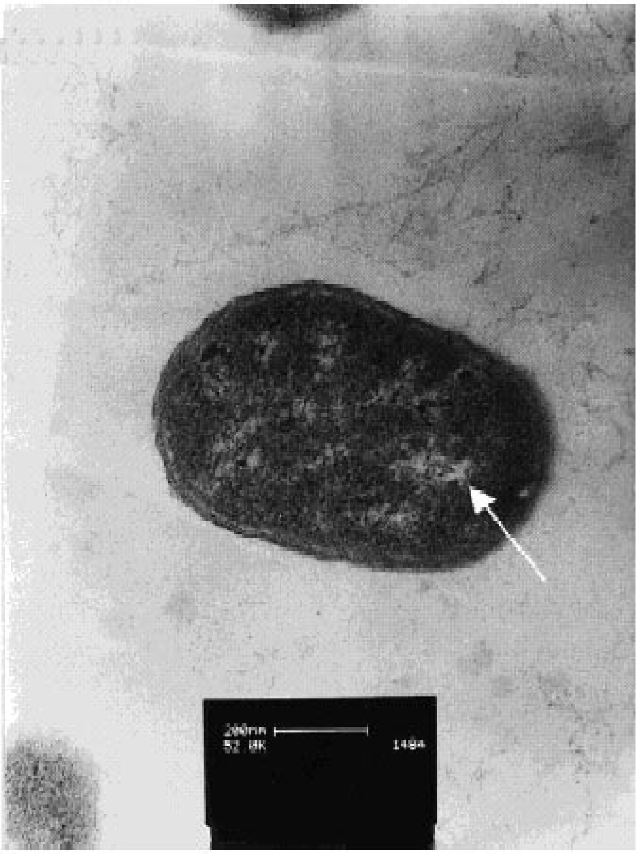

Fig. 1. Internal structure of the untreated *E. coli* cells.

Fig. 2. Internal structure of treated *E. coli* cells.

Table 1. **Solubility and Solubility Products of Silver(I) Compounds**

Silver(I) compound	CAS Registry Number	Aqueous solubility[a], g/L H_2O	K_{sp}[a]
acetate	[563-63-3]	1.1×10	
azide	[13863-88-2]		2.9×10^{-9}[b]
bromate	[7783-89-3]	1.6[b]	
bromide	[7785-23-1]	1.3×10^{-4}	3.3×10^{-13}
carbonate	[534-16-7]	3.3×10^{-2}	8.2×10^{-12}
chlorate	[7783-92-8]	9.0×10[b]	
chloride	[7783-90-6]	1.9×10^{-3}	1.8×10^{-10}
chromate	[7784-01-2]	3.6×10^{-2}	1.9×10^{-12}[b]
cyanide	[506-64-9]	2.3×10^{-5}	1.6×10^{-14}
fluoride	[7775-41-9]	1.8×10^{3}	
iodate	[7783-97-3]	4.4×10^{-1}[b]	3.1×10^{-8}[b]
iodide	[7783-96-2]	2.6×10^{-6}	8.5×10^{-17}
nitrate	[7761-88-8]	2.16×10^{2}[c]	
nitrite	[7783-99-5]	4.2	
oxide	[20667-12-3]	2.2×10^{-2}	
selenate	[7784-07-8]	1.2[b]	4×10^{-9}[b]
sulfate	[10294-26-5]	8.3	1.2×10^{-5}
sulfide	[21548-73-2]	1.4×10^{-4}[b]	1.0×10^{-50}[b,d]
			3.8×10^{-52}[e]
			5.9×10^{-52}[f]
sulfite	[13465-98-0]		2×10^{-14}[b]
thiocyanate	[1701-93-5]	1.3×10^{-4}[b]	1.0×10^{-12}[b]

[a] At 25°C unless otherwise indicated.

[b] At 20°C.

[c] Value is per 100 g H_2O.

[d] Ref. 7.

[e] Ref. 8.

[f] Ref. 3.