(4) *Chloride of Silver* (AgCl) comes down as a precipitate when solutions of silver salts are mixed with solutions of chlorides (for preparative purposes AgNO3 with HCl, which is preferable to NaCl). The mixture at first has the appearance of a milk, but on being violently shaken it divides into a curdy, heavy, easily settling precipitate and a clear solution,—more readily if the co-reagents are exactly balanced or the silver is in excess than when the precipitant predominates. Chloride of silver is as good as insoluble in water, but hydrochloric acid, and chloride solu­tions generally, dissolve it perceptibly. In dilute sulphuric and nitric acids it is as insoluble as in plain water. Even boiling oil of vitriol attacks it only very slowly. It is readily soluble in ammonia solution and reprecipitated therefrom on acidification. It dissolves in aqueous thiosulphate of soda, Na2S2O3, forming the very stable salt NaAg.S2O3, and in cyanide of potassium solution, forming KAg. (NC)2. From either solution the silver is conven­iently recoverable only by sulphuretted hydrogen or sulphide of ammonium as an Ag2S precipitate. Chloride of silver fuses at 260° C. into a yellowish liquid, freezing into a transparent, almost colourless, glass of horn-like consistence (hence the name “horn- silver ”). The specific gravity of frozen AgCl is 5∙45 (Karsten). It remains undecomposed, but volatilizes appreciably at a red heat. Hydrogen at a dull red heat reduces it to metal. A similar reduc­tion is effected in even the compact chloride by contact with zinc, water, and a little dilute sulphuric acid ; the reduction, however, proceeds rather slowly and is rarely quite complete. *Unfused* chloride of silver, when exposed to sunlight, becomes at first violet, then darker and darker, and at last black, through progressive de­chlorination. Yet even the black final product, according to Bibra, yields up no silver to hot nitric acid.

(5) *Bromide of Silver* (AgBr) closely resembles the chloride. The reduction on insolation is prevented by the presence of a trace of free bromine and promoted by that of nitrate of silver. Chlorine converts the hot fused salt into chloride.

(6) *Iodide of Silver* (AgI), while similar on the whole to the other two haloids, presents marked peculiarities. As formed by precipitation it is distinctly yellow ; it is insoluble in, but decol­orized by, ammonia ; it is less soluble in water and dilute nitric acid or other nitrate solutions than even the bromide, this latter exceeding in this sense the chloride. But boiling oil of vitriol decomposes it slowly, with elimination of iodine vapours and forma­tion of sulphate. Hydrogen at a red heat does not act upon it ; nor is it at all easily decomposed by zinc and dilute acid. Pre­cipitated iodide of silver is characteristically soluble in solutions of alkaline iodides and in those of nitrate of silver, with forma­tion of double salts, which, however, are all decomposed, more or less completely, by addition of much water. *Pure* iodide of silver, even if recently precipitated, is not changed by sun­light, but if contaminated with nitrate of silver it readily blackens. For action of light on silver haloids, see Photography.

Analysis.—In a solution of salts derived from purely oxygenated acids the least trace of silver can be detected by hydrochloric acid, which precipitates the silver as chloride (see above). The precipitate, when produced in a possibly complex solution, may include the chlorides of lead (PbCl) and mercurosum (Hg2Cl2). Repeated treatment of the (washed) precipitate with boiling water extracts the lead chloride ; then by pouring ammonia on the precipitate we convert the Hg2Cl2 into an insoluble black body, while the chloride of silver dissolves and, from the filtrate, can be precipitated by acidification. For the *quantitative* determination of silver, the ordinary laboratory method is to bring the metal into solution as nitrate and then to throw it down as pure chloride. The chloride is washed, collected, dehydrated by fusion, and weighed. According to Stas, if O = 16, Ag = 107∙93 and Cl = 35∙454 ; hence the chloride contains 0∙75273 of its weight of metal.

The *assaying* of silver ores is done preferably in the “dry way in fact relatively poor ores cannot be assayed satisfactorily in any other. The general method with sulphureous ores is to mix them, as powders, with (silver-free) oxide of lead and tartar, and fuse in a clay or graphite crucible. The regulus includes all the silver. The fuse is poured into a conical mould of cast- iron, when the metal goes to the bottom of the mould ; the ingot, after cooling, is easily separated from the adhering slag. The slag-free regulus is then placed in a little cupel made out of com­pressed bone-ash, and is heated in a muffle to redness and kept at this temperature in the current of air which pervades the muffle in virtue of its disposition in the furnace until all the lead and base metals generally have been sucked up by the porous cupel. The remaining “button” of metal is weighed, which gives the conjoint weight of the silver and gold, which latter metal is rarely absent. For its determination the button is rolled out into a piece of thin sheet, which is “parted” with nitric acid (see Gold). The gold remains and goes to the balance ; the weight of the silver is found by difference. Similarly, to determine the fineness of silver alloys, a known weight of the alloy—customarily 0∙5 gramme—is “cupelled,” with addition of a proportion of pure lead depending on the weight of base metal to be removed, as shown by

the following table, which, however, holds strictly only for copper- silver alloys :—

|  |  |
| --- | --- |
| Fineness 1000-900.......... | 80 units of lead per unit of copper. |
| „ 900-850......... | 64 ,, |
| „ 800-750......... | 53 ,, |
| ,, below 750......... | 50–40 ,, |

In a well-appointed laboratory two operators who work into each other’s hands can easily make several dozen of such assays in a day. Cupelling, indeed, is the promptest of all methods of ana­lysis, only the results are not quite as exact as is desirable in the case of precious metal, part of the silver being lost by volatilization, and part by being sucked into the cupel. The error attains its maximum in the case of alloys of about 700 per mille, and with these conies to about 1/150th of the weight of the silver to be determined. It of course can be, and always is being, corrected to some extent by “blank” assays made with known weights of pure silver and pure copper; but such corrections are not quite safe. Hence cupellation nowadays, in the mints at least, is used only for a first approximation, and the exact fineness determined by the “ wet-way ” process, invented by Gay-Lussac. See Assaying, vol. ii. p. 727.

A most excellent method for the quick determination of a not approximately known weight of dissolved silver has been invented by Volhard. This method rests on the fact that solutions of sulphocyanates (including that intensely red salt Fe(NCS)3 which is produced when, for instance, NCS.H is mixed with ferric sul­phate) precipitate silver completely from even strongly acid solu­tions, as NCS.Ag. A convenient reagent for the method is pro­duced by dissolving 1/10 NCS.NH4 grammes of (chlorine-free) sulphocyanate of ammonium in water to 1000 c.c. to produce a solution of which 1 c.c. precipitates about 1/10 Ag = 10∙8 milligrammes of silver. To determine the exact “titre,” we dissolve, say, 540 milli­grammes of pure silver in 1∙2 nitric acid, and next boil away every trace of N2O3. We then dilute to say 50 c.c., add 5 c.c. of saturated solution of iron alum (not less), and, lastly, run in sulphocyanate from the burette, until the red colour of ferric sulphocyanate which appears locally from the first, by addition of the last drop of NCS solution, has become permanent on stirring. Supposing 49∙3 c.c. of solution to have been required to reach this point, every 1 c.c. of reagent precipitates 540/493 milligrammes of silver, and it, of course, always does so, even, let us add, in the presence of (say) 70 per cent. of copper beside 30 of silver in the alloy under operation. Volhard’s method is more exact, and, with a small number of samples, takes even less time, than cupellation. (W. D. )

*Mode of Occurrence.—*Silver is rarely found in the native state, and then only in comparatively small quanti­ties. Most of the ores of silver are difficult to reduce, and it is therefore deemed safe to regard this as the last of the three great coining metals which came into use. Silver is originally as widespread as gold, occurring in nearly all the volcanic rocks and some of the Primary ones. In the Silver Reef district of Utah it is found in sedimentary sandstone, though this appears to have undergone some change from volcanic action. But gold remains unaltered by the action of the elements, and is often carried away long distances from its original place of occurrence by the breaking down of the rocks which contain it and their formation anew elsewhere, either as other rocks or as “placers” of gravel or sand, containing gold easily washed out by hand or with rude appliances. Silver, on the contrary, is only to be found in the rocks where it originally occurs. When these are broken down or worn away, the silver is either driven into new mineral combinations, or, more commonly, dissipated and lost. Hence silver is only to be obtained by subterranean mining, and demands the aid of capital and associated labour. The greater rapidity with which gold can be obtained has often influenced the legal relation of value between these two metals, and its bearing upon prices, commerce, and civilization.

*Cost of Production.—*In nearly all silver ores there is some gold, and in nearly all gold ores some silver. In the £70,000,000 worth of metal produced from the Comstock lode of Nevada nearly one-half in value consisted of gold. For this and other reasons, it is impossible to determine the general average cost of producing gold and silver from all the mines during any reasonably long period of time. If recent statistics are to be trusted, both metals are pro­