and the thorough coagulation by gentle boiling of any silver halide which may be formed at this point.

3. The addition of enough of some reducing agent to cause a rapid and total reduction of any oxyacids which may have been formed. Hydrazine sulfate was found to be far better than any other reducing agent which was tried.

4. This method is applicable to the highly halogenated and liquid compounds as well as to others.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, THROOP COLLEGE OF TECHNOLOGY.]

THE DETERMINATION OF SILVER IN ORGANIC COMPOUNDS.

BY H. J. LUCAS AND A. R. KEMP.

Received June 26, 1917.

The determination of silver in those salts which are completely soluble in water, or in nitric acid, is easily accomplished by precipitating the silver as chloride, and weighing as such. If the salt is insoluble in water, and gives, when treated with acids, an insoluble organic compound, the chloride precipitation method cannot be used.

A very simple method is to heat the silver salt of the organic acid, whereby a residue of metallic silver remains. Compounds containing nitrogen or sulfur also give metallic silver upon ignition, but when sulfur is present, the heating must be continued until the silver fuses.[1] This method is not applicable to halogenated silver salts.

The method of Carius,[2] in which the substance is decomposed by heating with concentrated nitric acid in a sealed tube at a high temperature, is of general application, and gives good results. However, Pelzer[3] has shown that certain substances are not completely oxidized by this treatment.

In the determination of silver in halogenated silver salts, Rindl and Simonis[4] modify the method of Carius by adding a potassium halide.

Dupont and Freundler[5] employ aqua regia as an oxidizing agent, the silver remaining as silver chloride. Recently Datta and Chatterjee[6] have shown that a large number of compounds, including many hydroxy derivatives, give chloropicrin and chloroanil when treated with aqua regia.

In the method of Vanino[7] the silver salt is converted into metallic silver by the reducing action of formaldehyde in strong alkaline solution.

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[1] Salkowski, *Ber.*, **26**, 2497 (1893).

[2] *Ber.*, **3**, 697 (1870).

[3] *Ann.*, **146**, 301 (1868).

[4] *Ber.*, **41**, 838 (1908).

[5] "Manuel Operatoire de Chimie Organique," p. 80 (1898).

[6] THIS JOURNAL, **38**, 1813 (1916).

[7] *Ber.*, **31**, 1763, 3136 (1898).

The Cyanide-sulfide Method.

Solutions of the alkali cyanides react with silver salts in general, forming the soluble argenticyanide complex and the alkali salt of the acid according to the general equation

$$AgA + 2Na^+ + 2CN^- = 2Na^+ + Ag(CN)_2^- + A^-.$$

The determination of the silver in the cyanide solution can be effected by precipitating it either as an insoluble silver salt, or as metallic silver. The method to be described depends upon its precipitation as sulfide, and estimation as such.

About 0.3 g. of the sample is weighed out into a 400 cc. beaker. Two or three drops in excess of the theoretical amount of 0.25 N sodium cyanide are added from a buret.[1] The solution is warmed, and as soon as the solid has dissolved, 10 cc. of 1 N sodium hydroxide are added, and the solution is diluted to 300 cc. About 25 cc. of 0.25 N sodium sulfide in excess of the theoretical amount required for the complete precipitation of the silver are then added slowly with stirring. The solution is heated to 60°, and stirred until the silver sulfide has coagulated. The precipitate is collected on a weighed Gooch crucible, and washed, first with water until free from sulfide, and finally with alcohol and ether. It is dried at 100–110° for one-half hour, and weighed. The heating is continued during fifteen-minute periods until the weight remains constant. More than two weighings are seldom necessary. The percentage of silver is calculated from the weight of silver sulfide.

If the accuracy of the method is to be limited by the sensibility of the ordinary analytical balance, not more than 0.05 mg. of silver should remain dissolved as argenticyanide. Taking silver oxalate as an example of a salt having a high silver content, the concentration of sulfide ion necessary to precipitate all except 0.05 mg. of silver from 0.3 g. sample can be calculated from the following equilibrium expressions: $(Ag^+)(CN^-)^2/(Ag(CN)_2^-) = 9.0 \times 10^{-22}$,[2] and $(Ag^+)^2(S^=) = 4 \times 10^{-50}$,[3] and is found to be 8.2×10^{-4} N. The value of the concentration of the complex ion is obtained by assuming that the 0.05 mg. of silver remains dissolved as argenticyanide.

In the analytical procedure given above, the concentration of sulfide ion above the silver sulfide precipitate may be calculated to be 2.2×10^{-3} N by taking the hydrolysis at 25° of 0.018 N sodium sulfide as 88%,[4]

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[1] Potassium compounds should be used if the sodium salt of the organic acid is insoluble. In case both sodium and potassium salts are insoluble, the cyanide solution can be filtered from the insoluble salt before the silver is precipitated as sulfide. However, some silver might be lost by being carried down with the precipitate.

[2] Bodländer, *Ber.*, **36**, 3934 (1904).

[3] Stieglitz, "Qualitative Analysis," Part I, p. 224 (1911).

[4] Küster and Heberlein, *Z. anorg. allgem. Chem.*, **43**, 71 (1905).

and assuming that the increase in hydrolysis caused by raising the temperature to 60° is offset by the effect of the sodium hydroxide added. Thus the procedure provides a concentration of sulfide ion somewhat greater than that calculated to be necessary even for a salt containing an unusually large percentage of silver. The results of analysis show also that it produces a quantitative separation of silver.

By combining the above mass action expressions, we find that $(S^=)/(CN^-)^4$ = Const. when the concentration of the argenticyanide ion is a constant. As the amount of cyanide which must be added is directly proportional to the amount of silver in the sample, the amount of sulfide necessary to give a quantitative precipitation will be proportional to the fourth power of the amount of silver. Therefore salts containing lower percentages of silver than silver oxalate, will require much less sulfide for the complete separation of the silver. However, since the precipitate of silver sulfide was observed to coagulate more readily when there is a considerable excess of sodium sulfide present, it is better to employ the amount specified.

Some advantages of this method are: Accuracy, speed, applicability and recovery of organic acid.

Its accuracy is demonstrated by some of the results obtained. Silver sulfide seems to have little tendency to carry down impurities. It showed no tendency to oxidize when dried at 110° for several hours.[1] On the basis of a 0.3 g. sample, 0.1 mg. of silver sulfide is equivalent to 0.03% silver. Analysis of some stable crystalline silver salts checked within this limit.

The operations involved, up to the time the crucibles are placed in the oven, require from one hour to one hour and a half.

The method should be applicable to all silver salts which are dissolved by sodium or potassium cyanide. Of a large number tried, only one, the silver salt of diazoaminobenzene, failed to dissolve in the 0.25 *N* sodium cyanide solution. The method has not yet been applied to the analysis of salts containing nitrogen and sulfur.

The recovery of the organic acid is accomplished by acidifying the filtrate from the silver sulfide with hydrochloric or sulfuric acid in a draught cupboard. If insoluble, the acid precipitates out and can be filtered off. This was done in the case of silver pentabromophenolate, mentioned below; one crystallization from alcohol gave a product which was as pure as the original preparation. If the acid is soluble in water, the hydrogen cyanide and hydrogen sulfide are driven out by boiling, after which the acid may be recovered by precipitating it as an insoluble salt, or by extracting with a suitable solvent. If considerable time has been spent in

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[1] Cf. Fresenius-Cohn, I, 200 (1912).

preparing and purifying compounds, a method which permits of their recovery after analysis possesses decided advantages.

The cyanide-sulfide method should lend itself to the analysis of cadmium salts also, since cadmium sulfide precipitates quantitatively from a cyanide solution.

Instead of precipitating the silver as silver sulfide, it is possible to reduce the argenticyanide solution to metallic silver with formaldehyde in alkaline solution. This problem is being investigated in this laboratory.

The cyanide-sulfide method is not applicable to salts which are insoluble in the cyanide solution. It probably will not work satisfactorily with those salts, the acids of which form insoluble sodium and potassium salts, or the acid radicals of which contain easily reducible nitro groups. In the latter case the reduction of the nitro group to an amino group will give rise to a weaker acid, which may be insoluble in the alkaline solution.

Experimental Part.

The following tables give the results of analysis of a few silver salts.

Analysis of Silver Oxalate.—The silver oxalate was prepared by adding 0.1 *N* pure silver nitrate to 0.1 *N* pure oxalic acid, with stirring. The white amorphous precipitate was protected from the light, and dried over phosphorus pentoxide *in vacuo* for several days. In spite of precautions the product was slightly acted upon by the light.

Sample.	Weight of sample	Weight of Ag_2S.	% Ag by analysis.	% Ag calc. from formula $C_2O_4Ag_2$.
I.	0.2832	0.2311	71.04	71.03
II.	0.3893	0.3178	71.09	...
III.	0.2523	0.2061	71.12	...

Analysis of Silver Benzoate.—Sodium benzoate was prepared by dissolving benzoic acid in 0.1 *N* sodium hydroxide, and the resulting solution was freed from chloride by adding a few drops of 0.1 *N* silver nitrate and filtering. The filtrate was treated with an equivalent mount of 0.1 *N* silver nitrate, and the precipitate of silver benzoate was crystallized three times from hot water. The product consisted of needle-like crystals which were slightly darkened, due to reduction, even though care was taken to protect them from the light.

Sample.	Weight of sample.	Weight of Ag_2S.	% Ag by analysis.	% Ag calc. from formula $C_7H_5O_2$ Ag.
I.	0.3187	0.1727	47.18	47.12
II.	0.3263	0.1762	(47.01)[1]	...
III.	0.4475	0.2429	47.23	...

Analysis of Silver Cinnamate.—Pure recrystallized cinnamic acid, m. p. 132.5° was carefully neutralized with a dilute solution of sodium hydroxide, which contained a small amount of chloride. The resulting solution was freed from chloride by adding a few drops of 0.1 *N* silver nitrate, and fil-

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[1] A few specks of Ag_2S were lost during filtration.

tering. From this point the operations were the same as in the preparation of silver oxalate, yielding finally a snow white amorphous product.

Sample.	Weight of sample.	Weight of Ag_2S.	% Ag by analysis.	% Ag calc. from formula $C_9H_7O_2$ Ag.
I	0.2866	0.1390	42.22	42.32
II	0.2722	0.1321	42.25	...
III	0.2734	0.1327	42.26	...

Analysis of Silver Anisate.—The salt was prepared from pure anisic acid, m. p. 185°. The operations were the same as those used in the preparation of silver benzoate. The product after five crystallizations was still slightly pink.

Sample.	Weight of sample.	Weight of Ag_2S.	% Ag by analysis.	% Ag calc. from formula $C_8H_7O_3$ Ag.
I	0.2438	0.1164	41.57	41.66
II	0.2400	0.1147	41.61	...
III	0.2314	0.1107	41.65	...

Analysis of Silver Pentabromophenolate.—A study of the different forms of this salt is being carried on by the authors. The details of preparation will be described in a future publication. The following results are given as an example of several very satisfactory analyses obtained during the course of the investigation:

Sample.	Weight of sample.	Weight of Ag_2S.	% Ag by analysis.	% Ag calc. from formula C_6Br_5O Ag.
I	0.3457	0.0781	18.10	18.11
II	0.4492	0.0935	18.12	...
III	0.2806	0.0584	18.12	...

Summary.

The cyanide-sulfide method for determining silver in organic compounds is discussed, and several typical analyses are given.

The method is shown to be a valuable one because of its applicability, speed and accuracy.

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[CONTRIBUTION FROM THE CHEMISTRY SECTION, IOWA AGRICULTURAL EXPERIMENT STATION.]

THE OCCURRENCE AND SIGNIFICANCE OF MANNITOL IN SILAGE.

BY ARTHUR W. DOX AND G. P. PLAISANCE.

Received July 9, 1917.

Introductory.

In continuation of our investigation on the fermentation phenomena that occur during the first two or three weeks after corn is put into the silo, and the products resulting from this fermentation, the writers have attempted to account in part at least for the soluble sugar which disappears but cannot be recovered in the form of volatile acid, lactic acid,