

CCLXV.—*A Volumetric Method for determining Silver in the Presence of Halides and Cyanides.*

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Most rapid volumetric methods for the determination of silver depend upon quantitative precipitation of an insoluble salt, and are therefore applicable only when the silver is present as a simple soluble salt, which dissociates to give silver ions. Of these, several important methods differ only in the indication of the end-point of the precipitation of silver chloride. In Gay Lussac's method (*Ann. Chim. Phys.*, 1835, **58**, 218) titration is continued until no further turbidity is seen; modifications of procedure have been suggested by Hoitsema (*Z. physikal. Chem.*, 1896, **20**, 272), Lang and Woodhouse (*J.*, 1908, **93**, 1037), Pannain (*Gazzetta*, 1909, **39**, ii, 240), Dewey (*J. Ind. Eng. Chem.*, 1913, **5**, 209), and Debrun (*Ann. Falsif.*, 1914, **7**, 407). Potassium chromate (Mohr, *Annalen*, 1856, **97**, 335; Doughty, *J. Amer. Chem. Soc.*, 1924, **46**, 2707) and arsenate (Mohr, *loc. cit.*) have been used as indicators, and the adsorption of

dyestuffs by the precipitate has been utilised by Fajans and Hassel (*Z. Elektrochem.*, 1923, **29**, 495) and Fajans and Wolff (*Z. anorg. Chem.*, 1924, **137**, 221; see also Böttger and Schmidt, *ibid.*, 1924, **137**, 246).

The precipitation of many other salts has been used for volumetric determination, *e.g.*, iodide by Carnot (*Compt. rend.*, 1889, **109**, 177), Altnéder (*Metallurgie*, 1906, **3**, 292), Schneider (*J. Amer. Chem. Soc.*, 1918, **40**, 583), Hendrixson (*ibid.*, 1921, **43**, 858), Pawloff and Schein (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 943), Pisani (*Annal. Mines*, 1856, **10**, 83), and Andrews (*Amer. Chem. J.*, 1900, **24**, 256); thiocyanate by Volhard (*J. pr. Chem.*, 1874, **9**, 217; *Annalen*, 1878, **190**, 1), and modifications by Knorr (*J. Amer. Chem. Soc.*, 1897, **19**, 814), Rose (*J.*, 1900, **77**, 232), Hoitsema (*Z. angew. Chem.*, 1904, **17**, 647), Drechsel (*Z. anal. Chem.*, 1877, **16**, 351), Rosanoff and Hill (*J. Amer. Chem. Soc.*, 1907, **29**, 269), and Ivanoff (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 66; *Chem.-Ztg.*, 1913, **37**, 427); ferrocyanide by Quessaud (*J. Pharm.*, 1884, **10**, 260); and Lescœur (*Bull. Soc. chim.*, 1897, **17**, 140) similarly used the oxide.

When the silver occurs partly or wholly as halides, none of the foregoing methods can be applied. The only rapid volumetric method available depends upon the quantitative conversion of the insoluble silver salt to a soluble complex cyanide, by dissolving it in standard potassium cyanide solution, excess of the latter being determined by back titration with a standard silver nitrate solution until a slight permanent precipitate is formed (Liebig, *Annalen*, 1851, **77**, 102). A slight modification was introduced by Denigès (*Compt. rend.*, 1893, **117**, 1078), who carried out the titration in the presence of ammonia and potassium iodide (see also Rebière, *Bull. Soc. chim.*, 1915, **17**, 306; Eggert and Zipfel, *Ber.*, 1919, **52**, 1177; *Z. wiss. Phot.*, 1924, **22**, 209). A direct cyanide titration method was introduced by Maresco (*J. Ind. Eng. Chem.*, 1924, **16**, 945), but its application is limited, and according to Meidinger (*Z. wiss. Phot.*, 1925, **23**, 282), it is less satisfactory than the method as modified by Eggert and Zipfel (*loc. cit.*).

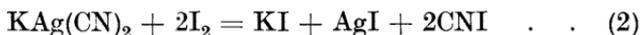
A rapid general method was required for the routine determination of silver occurring as halides in certain photographic products containing cyanides and small unknown and variable amounts of other substances which react with cyanide, for none of the known methods was directly applicable. Such a method was obtained by titration of a cyanide solution of the silver salt with iodine.

Previous iodometric methods of silver determination (Gooch and Bosworth, *Z. anorg. Chem.*, 1909, **62**, 74; Bosworth, *ibid.*, **64**, 189; Pawloff and Schein; Pisani; Andrews, *loc. cit.*) were applic-

able only to simple soluble salts of silver, but the method now described is of wider application. The principle is as follows. The silver is dissolved in a slight unknown excess of potassium cyanide solution. Standard iodine solution is run in until one drop produces a faint permanent opalescence of silver iodide, exactly as in cyanometric titrations. The excess of potassium cyanide has now completely reacted according to the equation



The first precipitation of silver iodide indicates the commencement of the decomposition of the potassium silver cyanide. Starch is added, and the titration with iodine continued until one drop produces a permanent blue colour. The silver complex has now completely reacted according to the equation



The volume of iodine added between the two stages determines the silver content, four atoms of iodine being equivalent to one atom of silver according to equation (2). Incidentally, the total iodine added defines the amount of cyanide present, since, from (1) and (2), $\text{CN}' \equiv \text{I}_2$.

In practice, it was found that the point of opalescence was better defined if an electrolyte was present, addition of 50 c.c. of 10% sodium chloride or potassium nitrate solution before the commencement of titration being found effective. It was thought possible that this end-point could be emphasised by dye adsorption so as to give an end-point analogous to those described by Fajans and his co-workers (*loc. cit.*). Since the end-point consists in the introduction of a precipitate of silver iodide into a solution containing excess of iodide ions, iodide "body" (see Fajans) must be formed, and hence the adsorbed dye must be basic in nature. No dye with suitable adsorbing properties could be found. The only basic dye mentioned by the originators of the method is rhodamine 6G, which gives a sharp colour change in acid solution, but in the alkaline or neutral solution essential for the present method no definite colour change could be obtained with this indicator.

During preliminary experiments, considerable difficulty was experienced owing to the presence of cyanogen iodide, which caused the development of a reddish coloration immediately before the starch end-point, and therefore made it impossible to detect the appearance of the blue colour within less than three or four drops of *N*/10-iodine solution. Indeed, a better end-point was given by the colour of the iodine alone, in the absence of starch. The difficulty was overcome, however, by diluting the liquid to be

titrated, whereby, owing to a difference in persistence, the formation of the reddish colour could be eliminated. 10 C.c. of $M/5$ -potassium cyanide ($N/10$ with regard to silver nitrate by Liebig's method) per litre was found to be the maximum cyanide-ion concentration consistent with a sharp end-point (one drop), the formation of the reddish colour being then negligible.

Lastly, the solution to be titrated must not at any stage approach acidity, for the reactions are far from quantitative even in faintly acid solution. The potassium cyanide solution is therefore made alkaline by the addition of 5 c.c. of ammonia (d 0.880) per litre, which also facilitates dissolution of silver compounds and has certain physiological advantages (Maresco, *loc. cit.*). A considerable degree of alkalinity may prevail without risk of causing reaction between iodine and alkali. In the absence of added alkali, although quantitative results were obtained by dilution with tap water (p_H 7.7), dilution with distilled water (p_H 6.0) gave inaccuracies of 2—3%.

Procedure.—The solutions required are: (1) Approximately $M/5$ -potassium cyanide solution, containing about 13 g. of potassium cyanide and 5 c.c. of ammonia (d 0.880) per litre. (2) $N/10$ -Iodine solution in potassium iodide, standardised, preferably by this method, against silver nitrate solution.

A quantity of material containing 0.05—0.09 g. of silver is dissolved in 5—9 c.c. of cyanide solution in a large beaker, 10% sodium chloride solution (50 c.c.) is added, and $N/10$ -iodine solution run in from a burette until separation of silver iodide causes a faint permanent opalescence. This starting point for the silver determination is definable to one drop of iodine solution with ordinary care; if the point is over-run, it may be readjusted after addition of a little cyanide solution, a known quantity being added if cyanide is also to be determined.

The solution is now diluted to 900—1000 c.c. with tap-water, and 5 c.c. of 0.5% starch solution are added: if more cyanide than the quantity recommended is present, the solution should be diluted correspondingly. The titration is continued until a permanent blue tint is obtained, definable to one drop with ease, and the volume of iodine added during this stage determines the quantity of silver present, since $A \equiv 2I_2$.

Examination of Fundamental Reactions.—The fundamental reactions underlying the method have been investigated both qualitatively and quantitatively, but no products of reaction other than those to be expected from equations (1) and (2) could be isolated. Quantitative experiments proved that the reactions between iodine and (i) potassium cyanide and (ii) the complex cyanide were in

accordance with the suggested mechanism to an accuracy of 0.1%, provided either that the cyanide were rendered alkaline with ammonia as recommended, or that the diluent water had $p_H > 7.5$.

Results.—The following results of determinations of silver and cyanide in mixtures of standard solutions and in photographic products illustrate the accuracy of the method.

A. *Known mixtures.* Known quantities of silver nitrate were treated with excess of alkali halides, and dissolved in excess of potassium cyanide, and silver and cyanide were then determined by the method described, the amount of dilution being roughly adjusted to the quantity of cyanide present. *N*/10-Iodine solution was used for the first four determinations, and *N*/50-solution for the last three.

	Silver.			Potassium cyanide.		
	Present, g.	Found, g.	Error, %.	Present, g.	Found, g.	Error, %.
1.	0.1073	0.1075	+0.2	0.2390	0.2392	+0.1
2.	0.1073	0.1073	±0.0	0.2390	0.2390	±0.0
3.	0.1073	0.1073	±0.0	0.2390	0.2390	±0.0
4.	0.1073	0.1076	+0.3	0.2390	0.2392	+0.1
5.	0.02160	0.02160	±0.0	Unknown		
6.	0.02160	0.02164	+0.2	Unknown		
7.	0.02160	0.02164	+0.2	Unknown		
		Mean	+0.13		Mean	+0.05

B. *Photographic products.* The method has been in use in several allied laboratories during the past two years, its trustworthiness when applied to photographic materials having been established by numerous tests, of which the following is typical.

Strips of material cut across a roll were subdivided into areas of 1 sq. dem., and alternate areas were independently analysed in two different laboratories.

Silver found (mg. per sq. dem.) :

								Average.
Laboratory A.	22.4	21.85	21.8	21.6	21.7	22.0		21.89
„ B.		21.8	21.8	22.0	21.8	22.0	22.3	21.95

The variations between individual readings are known from other evidence to be due to local variations in coating weight, but the averages obtained in the two laboratories differ by only 0.14% from the mean.

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