296. *The Reaction between Aqueous Silver Nitrate and Cuprous Thiocyanate. An Indirect Argentometric Method for the Determination of Copper and a " Spot " Test for Silver.*

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The reaction between cuprous thiocyanate and aqueous silver nitrate has been studied for comparison with those of the cuprous halides, and as a possible volumetric method for determining copper. It has been found that two mols. of silver nitrate react with one of cuprous thiocyanate to produce a smoky-brown residue, which is shown to be an equimolecular mixture of finely divided silver with silver thiocyanate. Hence, cuprous thiocyanate and the cuprous halides react similarly with aqueous silver nitrate. This reaction can be used as an argentometric method for determining copper, the determination being carried out in neutral or ammoniacal solution. The conditions under which the cuprous salt is precipitated prevent interference by mercury, and silver in moderate amount does not interfere. The reaction has been developed as a " spot " test for silver.

If a thiocyanate is titrated with silver nitrate in presence of cuprous thiocyanate and an adsorption indicator, the colour assumed by the precipitate at the end-point disappears on standing. When cuprous thiocyanate is treated with aqueous silver nitrate it assumes a smoky-brown colour, and the supernatant liquid develops the colour and shows the reactions of bivalent copper. The residue gives reactions for silver and silver thiocyanate. With cuprous thiocyanate in excess it is possible to replace silver completely by copper, and *vice versa.* A quantitative examination of this reaction showed that 1 mol. of cuprous thiocyanate reacts with 2 of silver nitrate, and that the residue contains 1 atom of silver which can be dissolved out by dilute nitric acid, leaving 1 mol. of silver thiocyanate. A similar result is obtained by repeatedly extracting the residue with ammonium hydroxide to dissolve out the thiocyanate. Hence, the residue is either the sub-salt, Ag_2NCS, or an equimolecular mixture of silver thiocyanate with finely divided silver.

Vogel (*Phot. Mitt.*, 1899, **36**, 344) found that cuprous halides react with aqueous silver nitrate, producing similarly coloured residues which he considered to be silver sub-halides, but further examination of these substances showed that they are probably mixtures of normal halides with finely divided silver (Emszt, *Z. anorg. Chem.*, 1901, **28**, 346; Waterhouse, *Phot. J.*, 1900, **24**, 156). The evidence for the existence of other silver sub-salts is unsatisfactory.

X-Ray powder photographs of an air-dried sample of the smoky-brown residue show 11 rings with diameters characteristic of silver, and another 10 with diameters identical with those given by silver thiocyanate. Nevertheless, it has not been possible to effect a satisfactory separation of the constituents of the mixture by flotation, and only prolonged treatment of the residue with mercury extracts any silver. In addition, when the undried residue is soaked in ammonium hydroxide (1 : 1) for 2 days, only part of the silver thiocyanate dissolves.

It follows that the reaction of cuprous thiocyanate with aqueous silver nitrate is similar to that of the cuprous halides. This reaction is relatively slow at room temperature, but is accelerated by heating, about 2 hours' gentle boiling being needed to make 0·25 g. of dry, finely divided cuprous thiocyanate react completely. The rate also depends on the state of division of the cuprous salt, and freshly filtered, undried material is more reactive than the dried substance : 0·25 g., when added to excess of boiling silver nitrate, needs about 30 minutes for complete reaction.

When the reaction was used to determine copper volumetrically, the maximum error in 14 determinations with 0·3-g. samples of crystalline copper sulphate was ± 0·26% and in 22 determinations on 0·5-g. quantities ± 0·36%. Mercury is not precipitated under the conditions used to precipitate cuprous thiocyanate. Silver in moderate quantity does not interfere, and with an atomic ratio Ag : Cu = 2 : 1, the maximum error in 8 determinations was ± 0·30%.

This is a somewhat simpler argentometric method for determining copper than that proposed by Biazzo and Tanteri (*Ann. Chim. appl.*, 1935, **25**, 44), but it is possible to adapt the latter method to deal with cuprous thiocyanate, and a maximum error of ± 0·45% was obtained in 11 determinations of copper sulphate.

By using this reaction as a " spot " test for silver, it is possible to detect in bright daylight as little as 2·2γ of silver, and in sunlight 1·1γ, in one drop (0·05 ml.) of solution. If the test is carried out in a small tube with 0·5 ml. of solution, silver can be detected in a 0·0004*M*- or a 0·0001*M*-solution in bright daylight or in sunlight respectively. Lead neither interferes with nor reduces the sensitivity of the test, and interference by mercury can easily be overcome. Nitric acid in moderate concentration does not interfere.

EXPERIMENTAL.

" AnalaR " Chemicals were used without further purification. Cuprous thiocyanate was made as required by using hydroxylamine as reducing agent; it was filtered on to a layer of macerated filter-paper supported on a pad of glass-wool in a Gooch crucible. (With asbestos as filtration medium more silver nitrate was subsequently used than corresponds to theory.) When required dry, the cuprous salt was washed with alcohol and dried in an air oven at 120—130°.

Silver was determined by Volhard's method, the following standardised conditions being maintained throughout. To the silver nitrate were added 10 ml. of concentrated nitric acid, 4 ml. of a saturated solution of ferric alum, and sufficient water to make the volume up to 200 ml. As Holwech (*Tidsskr. Kjemi*, 1930, **10**, 78) reported that the presence of copper interferes with the end-point, blanks were determined, 25 ml. and 50 ml. of silver nitrate being used with addition of 0·3 g. or 0·5 g. of crystalline copper sulphate. The corrections found were 0·05 and 0·08 ml., respectively, of 0·1*N*-ammonium thiocyanate and these were applied throughout this work. Determination of copper, when required, was carried out iodometrically. In the determination of silver thiocyanate by potassium iodate, results, based on the iodate weighed out, are lower than theory by as much as 1%, so the iodate was standardised against silver thiocyanate obtained from known volumes of a standard solution of the ammonium salt. Undried silver thiocyanate reacts rapidly. The low results obtained are thought to be due to inability to wash nitric acid completely out of the precipitate. When ammonium thiocyanate is determined with iodate in presence of small amounts of nitric acid, low results are obtained, as shown by the following data : 10 Ml. of ammonium thiocyanate required 14·65 ml. of iodate; with addition of 1 ml. or of 0·2 ml. of *N*-nitric acid the titre decreased to 13·45 ml. or 14·15 ml., respectively, and even with 0·1 ml. of acid the titre was only 14·45 ml., or still 1·4% low.

Examination of the Reaction.—(a) *Qualitatively.* 0·5 G. of cuprous thiocyanate was boiled with 150 ml. (excess) of silver nitrate for 2 hours and the residue separated. Part of this was heated with dilute nitric acid (1 : 1) until no further colour change occurred; the remaining solid was filtered off, and dissolved by long boiling with nitric acid. The rest of the residue was exhaustively extracted with ammonia, and the residual grey solid dissolved in nitric acid. The resultant acid and ammoniacal solutions were submitted to qualitative tests.

(b) *Quantitatively.* 0·25 G. lots of cuprous thiocyanate, or the undried precipitates of thiocyanate resulting from 0·3—0·5 g. portions of crystalline copper sulphate, were boiled with 50 ml. or 75 ml. of standard silver nitrate for 1—2 hours, filtered, and excess silver nitrate determined. Then in a few cases copper was also determined. Silver was dissolved out of the residue by heating on a water-bath for ½ hour with nitric acid (*d* 1·12), which does not attack silver thiocyanate, and determined; the silver thiocyanate in the remaining solid was also determined.

Determination of Copper Argentometrically.—The known weights of crystalline copper sulphate were converted into cuprous thiocyanate by Krauss's procedure (*Z. angew. Chem.*, 1927, **40**, 354). The precipitate and filter were added to a suitable volume of standard silver nitrate, previously made air free, and boiled gently for ½ hour, or an hour if the thiocyanate had stood overnight prior to filtration. After separation of the residue, excess silver nitrate was determined.

Modification of Biazzo and Tanteri's Method.—The apparatus was substantially that used by these authors (*loc. cit.*). A convenient volume of standard silver nitrate was made air free, the cuprous thiocyanate and filter added, and boiling continued for a few minutes, after which the closed flask was cooled by immersion in water. Then 10 ml. of concentrated ammonia were added without access of air, and the closed flask was heated on a water-bath for 15 minutes.

Finely divided silver was filtered off, well washed with dilute ammonia, and excess silver nitrate determined.

" *Spot* " *Test for Silver.*—A thin circular smear of freshly filtered cuprous thiocyanate was placed on filter-paper or porcelain, and the test solution dropped on it. The development of a brown coloration, changing to grey, was observed in the course of a few seconds. If porcelain was used, and the smear was exposed for 15 seconds 3″ below a 250-watt lamp with reflector, the sensitivity was the same as in daylight. Since much of the effectiveness of this test is lost unless the development of the coloration can be observed, no other artificial light sources were used. The test solution was also shaken in a small tube with a little undried cuprous salt; addition of too much cuprous salt retards the colour change. With the more dilute solutions the coloration tends to disappear on long exposure.

Moist cuprous thiocyanate alone was found to be non-sensitive to light under the conditions specified, and when solid ammonium thiocyanate was substituted for the cuprous salt, tests were negative even with 0·1*M*-silver nitrate.

Interference.—With 0·0004*M*-silver solutions the test was positive in sunlight so long as the concentration of nitric acid did not exceed 1·4*N*, but in a small tube the test failed when this concentration became greater than 0·5*N*. With sulphuric acid up to *N* instead of nitric acid, positive results were obtained. In a small tube a retardation in the rate of colour formation was noticeable, greater in the case of nitric acid, as the acid concentration increased. The more pronounced interference by nitric acid may be due to its greater solvent action on finely divided silver.

Dilute solutions of mercuric nitrate give a greenish-yellow coloration with a smear of cuprous thiocyanate. The mercury in a solution obtained by mixing 10 ml. of 0·1*M*-mercuric nitrate with 4 ml. of 0·01*M*-silver nitrate was precipitated by careful addition of ammonia, and filtered off. The ammoniacal silver solution was just acidified with acetic acid and diluted to 100 ml.; it then gave a positive test.

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