CCLXXI.—*The Use of Titanous Chloride in the Volumetric Estimation of Copper and Iron.*

By WILLIAM GIDLEY EMMETT.

IN the course of a research involving many analyses of cupric chloride solutions, copper was estimated in the solutions by titration with titanous chloride, ferric ammonium sulphate in known quantity and potassium thiocyanate in excess being added as indicator. The method is well known and is described by Knecht and Hibbert ("New Reduction Methods in Volumetric Analysis," 1918) and other workers.

A source of error, apparently hitherto unremarked, lies in the somewhat rapid decomposition of ferric and cupric thiocyanates by water at the ordinary and at higher temperatures. These reactions were investigated by Philip and Bramley (J., 1913, **103**, 795; 1916, **109**, 597), who showed that the salts were reduced; in the case of the ferric salt, the rate of reduction was diminished by acid when an excess of alkali thiocyanate was present, and greatly increased by a rise in temperature; but the rate of reduction of cupric thiocyanate was not investigated. The results of a brief study of these sources of error, in so far as they concerned the other research, are now reported.

The titrations were carried out according to the technique described by Knecht and Hibbert, carbon dioxide being passed through the flask. A 15% solution of titanous chloride, after being boiled with concentrated hydrochloric acid, was diluted to give an approximately 0·02*N*-solution, and stored in the apparatus depicted (*loc. cit.*). (The diluted solution contained as impurity about 0·00013 g. of iron per c.c. as determined by oxidising 5 c.c. of the original 15% solution with acidified potassium permanganate and titrating the resulting ferric salt with a standardised titanous chloride solution.) A solution of standardised (approx. 0·025*N*) acidified ferric ammonium sulphate was used for checking the titanous chloride solution before and after each series of titrations, a slight but continuous decline in strength being noted.

Decomposition of Ferric Thiocyanate.—Solutions of ferric thiocyanate, prepared by mixing 25 c.c. of ferric chloride solution of known strength with 10 c.c. of 10% potassium thiocyanate (A.R.), containing different quantities of hydrochloric acid were titrated with standard titanous chloride at various intervals after mixing. The results (Table I) show that the decomposition is slight at the

TABLE I.

Conc. of $Fe(CNS)_3$, *N*.	Acidity due to added HCl, *N*.	Temp.	Interval between mixing and titration (mins.).	Ferric salt reduced, %.
0·0184	nil	16°	3	<0·2
			6	0·5
			10	0·5
0·0184	nil	25	6	1·4
0·0189	nil	50	*ca.* 0·5	4·7
			1·5	11·5
			3	16·1
0·0189	0·43	50	*ca.* 0·5	1·7
			1·5	8·4
			3	12·9
*0·155	nil	25	12	5·1
			46	7·5
*0·155	0·25 (H_2SO_4)	25	15	2·5
			50	3·6

* Experiments by Philip and Bramley.

ordinary temperature, and (in agreement with Philip and Bramley) that it is more pronounced at higher temperatures, but is inhibited by acid. Consequently, in analytical work the titration of ferric thiocyanate solutions must be carried out at the ordinary temperature in the presence of free acid and without undue delay after addition of thiocyanate to the ferric salt.

Decomposition of Cupric Thiocyanate.—Titrations with titanous chloride after different intervals were made on portions of 25 c.c. of cupric chloride solution (A.R.) to which had been added as indicator 10 c.c. of 10% potassium thiocyanate (A.R.) and 5 c.c. of the standard ferric solution together with varying amounts of hydrochloric acid. Typical results are given in Table II.

TABLE II.

Conc. of $Cu(CNS)_2$, *N*.	Acidity due to added HCl, *N*.	Temp.	Interval between mixing and titration (mins.).	Cupric salt reduced, %.*
0·0151	Nil	16°	*ca.* ½	3·8
			2	6·6
			4	8·0
0·0144	0·09	Room temp.	2	<0·1
			6	0·7
0·0151	*ca.* 1·2	Room temp.	2½	0·2
			71	1·3

* Since the velocity of change of ferric thiocyanate at the ordinary temperature is seen to be small compared with that of cupric thiocyanate, the total reduction has been ascribed to the latter.

Solutions of cupric chloride containing hydrochloric acid in concentrations from 0·25*N* to 3·3*N*, when titrated at the ordinary temperature with titanous chloride as soon as possible after addition of potassium thiocyanate, gave results which agreed amongst themselves within 0·1%. It is thus seen to be essential in the titration of cupric thiocyanate solutions to observe the same precautions as in the case of ferric thiocyanate.

When solutions of cupric chloride (*ca.* 0·015*N*) and 10% potassium thiocyanate (with or without added acid) were mixed and kept for 10 minutes or more before titration with titanous chloride, sharp end-points were not obtained; after the red colour of the ferric thiocyanate indicator had yielded to a colourless solution holding a pale grey precipitate, it developed again in a few seconds. Further addition of a drop of titanous chloride caused decoloration followed by renewed appearance of colour, and so on. The phenomenon is ascribed to the precipitation of cupric thiocyanate from the solution while awaiting titration, black acicular crystals having been observed under such conditions; in the course of the titration the precipitate slowly redissolves and reacts at the end to re-form ferric thiocyanate.

This supplies another reason why titration of cupric thiocyanate solutions should be done without loss of time.

By following Knecht and Hibbert's method with the addition of the precautions mentioned, analyses with an error of less than 0·2% were easily obtained. The titanous chloride solutions were standardised against a solution of cupric chloride (A.R.) in which the chlorine had been determined gravimetrically as silver chloride and/or the copper as cuprous thiocyanate.

A more convenient method of preparing a standard copper solution consists in dissolving a known weight of electrolytic copper in a solution of sodium peroxide in hydrochloric acid. About 5 g. of sodium peroxide are added to about 20 c.c. water and the solution is acidified with concentrated hydrochloric acid, being kept cool meanwhile. About 1 g. of pure copper turnings is added and dissolves in about ½ hour. The solution is then boiled under reflux to decompose all hydrogen peroxide (or to drive off dissolved chlorine), and diluted to a convenient volume. This method gave results from 0·1 to 0·2% lower than that previously described, probably on account of the presence of traces of iron in the sodium peroxide used.

The use of ferrous ammonium sulphate as a primary standard has been adversely criticised by the U.S. Bureau of Standards (Circular No. 26, 1921, 11) and by Thornton and Wood (*Ind. Eng. Chem.*, 1927, **19**, 150), and the author's results are in agreement with this.

The reduction of solutions of cupric thiocyanate on standing gives a ready explanation of Tomiček's observation (*Rec. trav. chim.*, 1924, **43**, 798) that when copper sulphate solutions were titrated by the potentiometric method in the presence of an excess of potassium thiocyanate large divergences from the expected figures were obtained; his suggestion that the thiocyanate is changed to sulphide, the copper salt being thereby fixed, is probably incorrect.

Highly erratic results were also recorded by Mach and Lederle (*Landw. Versuchs-Stat.*, 1914, **84**, 142) when titrating mixtures of ferric chloride and cupric sulphate in the presence of potassium thiocyanate, the ascertained copper content of cupric sulphate crystals varying from 25·08 to 18·26% with increasing concentration of ferric salt, whilst analysis by the electrolytic method gave 25·52% copper. These vagaries may perhaps also be ascribed to decomposition of the thiocyanates prior to titration, or alternatively to precipitation of cupric thiocyanate from the solutions.

The author desires to express his indebtedness to Dr. S. R. Carter for valuable assistance in the course of the work.

THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, March* 31*st*, 1927.]