has been developed. The procedure is adapted to the analysis of liquids of widely varying water content.

2. It has been found that the reaction of acetyl chloride and pyridine with water is much more rapid than the corresponding reactions with alcohols and amines. Consequently a moderate excess of alcohol or amine over the stoichiometric amount generally does not interfere with the determination of water.

3. By means of the new method water has been determined successfully in over twenty different organic compounds including fatty acids.

4. Substances known to interfere with the method are discussed.

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A Modified Iodimetric Method of Determining Copper

BY H. W. FOOTE AND JOHN E. VANCE

The iodimetric method of determining copper consists essentially in treating a solution of the cupric salt with a soluble iodide which precipitates cuprous iodide and liberates iodine. The latter can be titrated with thiosulfate. The method has, however, certain difficulties which are familiar to those who have used the method, and which limit its accuracy. In particular, the reaction on which the method depends, $2CuI_2 \longrightarrow 2CuI + I_2$, which is reversible, does not run quite to completion when the iodine is titrated. This appears to be due partly to adsorption of iodine by cuprous iodide, which in consequence is distinctly colored instead of white at the end-point. The fact that cuprous iodide is not extremely insoluble also contributes to the difficulty of obtaining complete reaction. The method is, however, widely used on account of its speed but is hardly to be classed in accuracy with a number of other iodimetric methods. When used, the thiosulfate should be standardized with copper under rather definite conditions because of the lack of an exact stoichiometric relation between copper and iodine in the reaction.

A modification of this method was proposed by Bruhns[1] with the object of using less iodide than is necessary by the usual method. The modification consists in adding potassium thiocyanate along with the iodide, which precipitates the more insoluble cuprous thiocyanate instead of cuprous iodide. This modification has been shown repeatedly to give unreliable results and recently[2] the reasons for the failure of the method

have been investigated in considerable detail. Briefly, the modified method gives low results because both iodine and thiocyanogen are liberated simultaneously to a certain extent, and react on each other.

In principle, however, the Bruhns method has one advantage, since cuprous thiocyanate is more insoluble than cuprous iodide, thus tending to make the reaction more complete due to the more complete removal of cuprous ion. As we have found in the present investigation, moreover, cuprous thiocyanate does not adsorb iodine at low concentrations of the latter, but becomes white as the free iodine is removed by titration, which makes the end-point exceedingly sharp in the presence of starch. It appeared probable that the undesirable side reactions occurring in the Bruhns method could be eliminated by adding the soluble thiocyanate late in the course of the titration. In that case the method should have greater accuracy than the usual method. The qualitative effect of adding a thiocyanate can be shown very easily. If this salt is added, during a titration, just as the end-point is reached by the usual method, the starch iodide color is markedly intensified. Quantitatively, the additional iodine liberated when the thiocyanate is added at this point amounts to about 0.15 cc. of decinormal thiosulfate.

Experimental

The copper used in the determinations given below containing 99.955% of the metal, was kindly furnished us by the Department of Metallurgy of this University. The impurity consisted chiefly of oxygen. The two thiosulfate solutions used were standardized by means of resublimed iodine and the equivalent in copper calculated.

(1) Bruhns, Z. anal. Chem., 58, 128 (1919); 59, 337 (1920).

(2) Krüger and Tschirch, ibid., 97, 161 (1934). These writers also give complete references to the literature regarding the modified method of Bruhns.

Neither solution varied in strength while the determinations were in progress to an extent which could be detected. The potassium iodide used contained a trace of iodate or its equivalent which was detectable with starch when the solution was acidified. This would not affect the standardization of the thiosulfate but would affect the copper determination (due to the acidity of the solution). A small correction (0.01 cc. per gram of iodide) was applied in all cases for this impurity in titrating the copper samples. Determinations were made both with a volume and a weight buret. The errors in weight of copper found are about the same by both methods, indicating that the major error is in estimating the end-point rather than in measuring the amount of thiosulfate. The percentage error by the weight buret is somewhat less than by the other, as larger weights of copper could be used.

In all determinations, the initial treatment was the same. The weighed sample of copper was dissolved in nitric acid, 5 cc. of 6 N sulfuric acid was added and nitric acid removed by evaporation. After dissolving in 20 cc. of water, 2-3 g. of potassium iodide was added and the titration carried out as in the usual method till most of the free iodine was exhausted. After adding starch solution, the titration was continued nearly to the end-point usually obtained. At this point, approximately 2 g. of ammonium thiocyanate was added and dissolved by thorough stirring. The starch iodide color immediately deepens. The end-point is exceedingly sharp, the precipitate turning white. The explanation of the white precipitate at the end-point instead of the usual slightly brownish precipitate appears to be that the cuprous iodide is transformed, at least on the surface of the particles, into the more insoluble thiocyanate, liberating the small amount

TABLE I

Copper sulfate + sulfuric acid ≡ 5 cc. H_2SO_4. Volume before titration 20 cc. In nos. 1-8, 2 g. of KI added in each determination and a volume buret used. Thiosulfate, 0.08976 N. In nos. 9-21, 3 g. of KI added in each determination and a weight buret used. 1 g. of thiosulfate = 0.012842 g. of I = 0.0064315 g. of Cu.

No.	Pure Cu taken, g.	Thiosulfate used	Cu found, g.	Error
1	0.2521	44.22 cc.	0.2523	+0.0002
2	.2301	40.43 cc.	.2307	+ .0006
3	.2401	42.10 cc.	.2402	+ .0001
4	.2505	43.90 cc.	.2505	.0000
5	.2320	40.61 cc.	.2317	− .0003
6	.1378	24.18 cc.	.1380	+ .0002
7	.1176	20.69 cc.	.1181	+ .0005
8	.1618	28.38 cc.	.1619	+ .0001
9	.3267	50.824 g.	.3269	+ .0002
10	.3710	57.754 g.	.3714	+ .0004
11	.3709	57.671 g.	.3709	.0000
12	.2922	45.361 g.	.2917	− .0005
13	.3286	51.060 g.	.3284	− .0002
14	.3053	47.497 g.	.3055	+ .0002
15	.3086	47.988 g.	.3086	.0000
16	.3019	46.959 g.	.3020	+ .0001
17	.3160	49.190 g.	.3164	+ .0004
18	.3132	48.731 g.	.3134	+ .0002
19	.4261	66.338 g.	.4267	+ .0006
20	.3771	58.695 g.	.3775	+ .0004
21	.3316	51.644 g.	.3321	+ .0005

of adsorbed iodine. This low concentration of iodine is not adsorbed by the cuprous thiocyanate. Table I gives the results of the first series of determinations.

In the usual iodimetric determination of copper, the titration is commonly carried out in a solution of acetic acid buffered with an acetate, although Whitehead and Miller[3] have recently shown that considerable concentrations of hydrogen ion have but little effect on the titration. The determinations in Table II were made like those in Table I, except that to each solution about 3 g. of ammonium acetate was added, to reduce the hydrogen ion concentration, before the addition of potassium iodide.

TABLE II

Conditions like those in Table I with the addition of 3 g. of ammonium acetate before adding potassium iodide. In nos. 1-8, the volume buret was used; in nos. 9-12, the weight buret.

No.	Pure Cu taken, g.	Thiosulfate used	Cu found, g.	Error
1	0.1571	27.55 cc.	0.1572	+0.0001
2	.1985	34.78 cc.	.1985	.0000
3	.2795	48.98 cc.	.2795	.0000
4	.1399	24.55 cc.	.1401	+ .0002
5	.1814	31.80 cc.	.1815	+ .0001
6	.1986	34.80 cc.	.1986	.0000
7	.1811	31.82 cc.	.1816	+ .0005
8	.2652	46.48 cc.	.2652	.0000
9	.3404	52.974 g.	.3407	+ .0003
10	.3210	49.948 g.	.3212	+ .0002
11	.3387	52.689 g.	.3389	+ .0002
12	.3216	50.022 g.	.3217	+ .0001

The errors shown in Table II are of the same order as those in Table I, showing that very considerable changes in hydrogen-ion concentration have no measurable effect on the accuracy of the method. This corresponds with the conclusions of Whitehead and Miller[3] on the unmodified iodimetric method.

Taking all the results of Tables I and II, by the volume buret, the error in determining 3.22 g. of copper amounted to +0.0023 g. or 1 part in 1400; by the weight buret, the error on 5.69 g. of copper was +0.0031 or 1 part in 1800. Within these limits, the results show that the reaction between a cupric salt and potassium iodide runs to completion in stoichiometric proportions by the method outlined above. The method appears to be comparable in accuracy with the best iodimetric methods.

Dilution of the solution before titrating has little effect on the result. Using an initial volume of 200 cc. (instead of 20 cc.) two deter-

(3) Whitehead and Miller, *Ind. Eng. Chem., Anal. Ed.,* 5, 15 (1933).

minations on about 0.2 g. of copper each, gave, respectively, errors of +0.0002 and −0.0004 g. The presence of nitric acid in small amounts also has no effect. Adding 1 cc. of concentrated nitric acid in each of two determinations, in an initial volume of 20 cc., one (using a volume buret) gave an error of +0.0003 g. and the other (weight buret) an error of +0.0002 g. This is of interest merely in showing that the complete elimination of nitric acid is unnecessary in the first evaporation with sulfuric acid, an operation which is sometimes troublesome on account of spattering.

Summary

A modification has been suggested, in the iodimetric determination of copper, which consists in adding a soluble thiocyanate near the end-point of the usual titration. Under these conditions, a further small liberation of free iodine occurs, and the reaction runs to a very sharp end-point. The precipitate at the end-point is white. The reaction takes place in stoichiometric proportions within about one part in sixteen hundred, so that the method appears to be comparable in accuracy with the best volumetric methods.

The Solubility of Helium in Water at 0, 25, 50 and 75° and at Pressures to 1000 Atmospheres[1]

BY R. WIEBE AND V. L. GADDY

The solubility of helium in water was measured for the purpose of obtaining a more general picture of the behavior of gases in water solution. The apparatus and method have been described previously.[2] The helium was 99.95% pure and was furnished by the Amarillo Helium Plant of the U. S. Bureau of Mines. It was found that a 1% nitrogen impurity had a very decided effect in raising the solubility but that the effect due to 0.05% was well within our experimental error. The results are given in Table I. Two or three series of runs were made at each temperature and pressure. Each series is represented by a line of figures in the table. The probable errors were estimated in the usual fashion from the equation

$$E = 0.674 \sqrt{\Sigma\Delta^2/n(n-1)}$$

The partial pressures in column 1 were calculated as follows: Using the Poynting relation[3] the effect of the gas pressure on the vapor pressure of water was determined. These calculated vapor pressures were used to correct the measured total pressure for the presence of water vapor. Since the vapor pressures of water at 0, 25, 50 and 75° are 0.006, 0.031, 0.12 and 0.38 atm., respectively, the correction even at 75° and 1000 atm., where

the worst deviation might be expected, would hardly be more than a few hundredths of 1%.
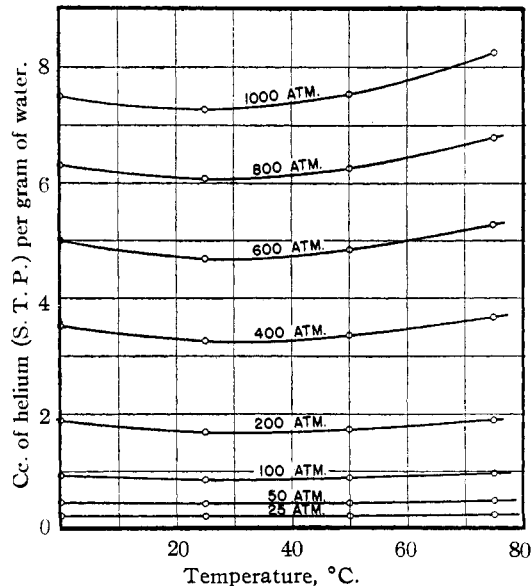

Fig. 1.

The main sources of error are in the sampling procedure and in measuring the exact equilibrium pressure. The solubility isobars in Fig. 1 show the same general trend with temperature as nitrogen and hydrogen.[2,4]

(1) Read at the meeting of the American Chemical Society, New York City, April 23-27, 1935.

(2) Wiebe, Gaddy and Heins, THIS JOURNAL, 55, 947 (1933).

(3) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 183.

(4) Wiebe and Gaddy, THIS JOURNAL, 56, 76 (1934); Saddington and Krase, ibid., 56, 353 (1934).