

sion discussed with special reference to the author's modification of the method of capillary rise.

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THE DETERMINATION OF CHLORIDES BY MEANS OF A CALORIMETRIC TITRATION AND SOME EXPERIMENTS ON THE TITRATION OF MIXTURES OF CYANIDE AND HALIDES¹

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The experiments described in this article were undertaken with a view to determine the applicability of a calorimetric titration to the analysis of chlorides and mixtures of cyanide and halides. The apparatus used and the methods of procedure were similar in most respects to those employed by Dean and Watts² in the calorimetric determination of sulfur, except for the following modification: tap water at approximately 12.5° was made to flow through the glass jacket surrounding the buret. The solutions to be titrated were cooled to a temperature slightly below that of the standard solution. When this procedure was followed, more uniform results were obtained than when the titrations were carried out at room temperature without the water-jacketed buret.

Standardization of Silver Nitrate Solution

An approximately 0.5 *N* solution of silver nitrate was titrated calorimetrically against weighed portions of carefully purified samples of potassium chloride.

Determination of Chlorine in Soluble Chlorides

Six samples of mixtures containing soluble chlorides were titrated using the standard silver nitrate solution. The results of these titrations are given in Table I.

TABLE I
DETERMINATION OF CHLORIDE WITH STANDARD SILVER NITRATE SOLUTION

Sample	Calorimetrically		Gravimetrically	
1	20.36	20.07	20.34	20.31
2	34.51	34.32	34.42	34.74
3	22.97	22.76		23.04
4	25.13	25.35	24.97	25.30
5	20.24	20.40	20.13	20.31
6	39.95	40.36	40.30	39.95

¹ Adapted from a thesis submitted by Evelyn Newcomer in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Colorado.

² Dean and Watts, THIS JOURNAL, 46, 854 (1924).

Titration of Mixtures of Halides and Cyanides

A consideration of the solubilities and heats of formation of the silver halides and cyanide leads one to expect in the curves breaks representing the complete precipitation of the respective salts—assuming that simultaneous precipitation does not take place. Thus it should be possible to determine the halides and cyanide when present in a mixture. In order to test this hypothesis 2% solutions of potassium cyanide and sodium

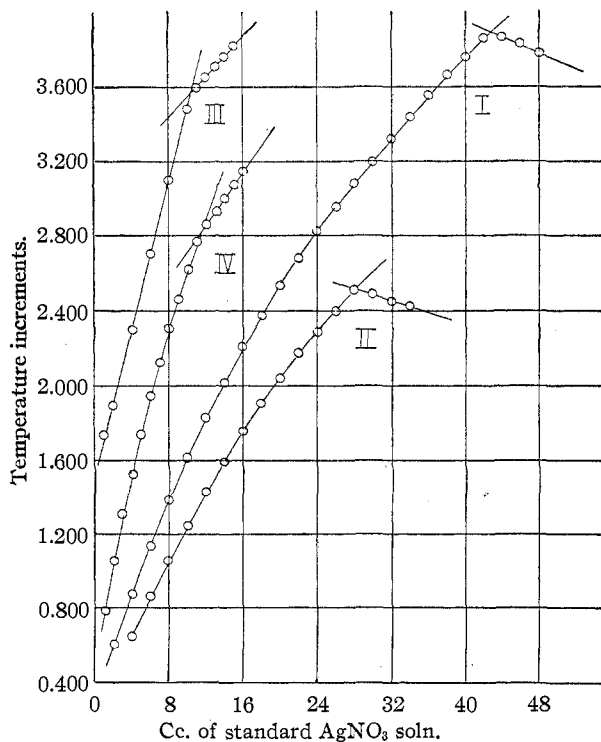


Fig. 1.—Titration of mixtures of halides and cyanide.

chloride were prepared and mixtures of these titrated. The results of two titrations are shown in Fig. 1. Curve I represents a mixture of 10 cc. of potassium cyanide and 50 cc. of sodium chloride solution. Curve II was obtained by plotting the results of the titration of a mixture of 20 cc. of potassium cyanide and 20 cc. of sodium chloride solutions. In each case the only break in the curve falls at the point of complete precipitation of both cyanide and chloride. Curve III resulted from the titration of a solution of cyanide alone. This is similar to the curves obtained for pure chlorides.

A solution containing 0.2005 g. of potassium chloride, 0.2005 g. of potassium bromide and 0.2001 g. of potassium iodide was prepared and

titrated. On plotting the data for this titration Curve IV, Fig. 1 resulted. This is similar in form to Curves I and II. Here again the only break found occurs at the point representing complete precipitation of the insoluble salts. The amount of standard solution required for titration was 11.22 cc., while the calculated amount is 11.125 cc.

Determination of Halogen in Organic Compounds

Dains and Brewster³ have described a method for the determination of halogens in organic compounds in which the substance to be analyzed is dissolved in liquid ammonia and treated with sodium. They observed

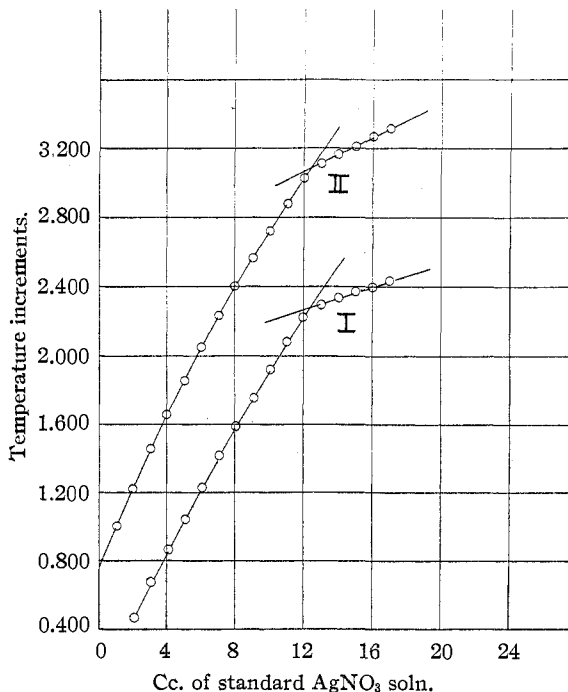


Fig. 2.—Determination of chlorine in dichloro-aniline.

that in certain cases (in the analysis of chloroform, for example) considerable amounts of cyanide were formed.

Samples of chloroform were treated according to the directions given by Dains and Brewster and titrated calorimetrically. When the data were plotted, curves similar in all respects to I and II of Fig. 1 were obtained.

Following the same procedure with dichloro-aniline, in which no cyanide should be formed, the curves shown in Fig. 2 were plotted. In this case the calculated percentage of chlorine was 43.78, while 43.90% was found (Fig. 2, Curve I).

³ Dains and Brewster, *THIS JOURNAL*, **42**, 1573 (1920).

Summary and Conclusions

It has been shown that chlorides may be determined calorimetrically with a fair degree of accuracy when other ions capable of being precipitated by silver nitrate are absent. In cases where mixed halides, or halides and cyanide, are present in the solution, the total amount of standard solution used is indicated by a break in the curve. Breaks indicating the fractional precipitation of the insoluble salts do not appear. The method cannot be applied to the analysis of organic compounds by the decomposition in liquid ammonia when cyanides are likely to be formed, as with chloroform, carbon tetrachloride, etc.

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THE PREPARATION OF FREE HYDROXYLAMINE

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Until recently, the best way to isolate free hydroxylamine was by fractional vacuum distillation of a solution of hydroxylamine in methanol. Two years ago, Lecher and Hofmann¹ showed that hydroxylamine could be made to crystallize from absolute ethyl alcohol in a yield of 40%. This is comparable to the yield obtained by the older method. The great advantage of the crystallization method, however, is that there is no loss of hydroxylamine. The material which remains in solution after the recrystallization is easily recoverable. A few methods of recovery are listed in the work which follows.

It seemed reasonable that with the selection of a better solvent, the yield of free hydroxylamine might be increased. Lobry de Bruyn² showed that the solubility of hydroxylamine was much less in methanol than in water, less in ethanol than in methanol, and that it was insoluble in hydrocarbons. It was inferred that the longer the hydrocarbon chain of an alcohol, the lower would be the solubility of the hydroxylamine. Butyl alcohol, because of its longer hydrocarbon chain and because of its commercial availability, was a logical choice.

It was found that with butyl alcohol, a consistent yield of 50% of free hydroxylamine was attainable. In addition, several time-saving factors were introduced. Contrasted with the high purity required for ethyl alcohol, commercial butyl alcohol need be purified only by distillation; the fraction boiling at 115.5–117.5°, was used. Instead of cooling the

¹ Lecher and Hofmann, *Ber.*, **55B**, 912 (1922). See also, Houben, *J. prakt. Chem.*, [2] **105**, 20 (1922).

² De Bruyn, *Rec. trav. chim.*, **11**, 18 (1892).