from thionyl chloride is the same as that prepared from phosphorus pentachloride is confirmed, and it is shown that the acid chloride prepared from phosphorus trichloride is identical with the others since it gives the same methyl ester.

These experiments were carried out under the direction of Professor F. B. Allan.

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE HAWAII AGRICULTURAL EXPERIMENT STATION.]

ON THE DETERMINATION OF SMALL QUANTITIES OF HYDROCYANIC ACID.

BY MAXWELL O. JOHNSON.

Received April 10, 1916.

In connection with some recent chemical work on cassava, there developed a need for a rapid and accurate method for the determination of small quantities of hydrocyanic acid. The silver gravimetric method is not suitable for small amounts of cyanides, such as one milligram, and the reducing substances found in plant distillates interfere with this and the various titration methods. These reducing substances also interfere with the picric acid colorimetric method of Waller[1] as shown by Chapman.[2]

Moore[3] determines the hydrocyanic acid in cassava by heating 540 grams of pulped root in an iron retort for two hours, absorbing in potassium hydroxide solution the hydrocyanic acid distilled. The distillate is acidified with sulfuric acid and redistilled into water containing 5 cc. of tenth-normal potassium hydroxide. As the distillation proceeds, the distillate is titrated with tenth-normal silver nitrate and potassium hydroxide added as necessary, to provide for a minimum excess of potassium hydroxide present when the titration is completed. The method appears accurate but requires special iron retorts and a long distillation. The writer found when cassava was distilled into potassium hydroxide solution, that organic matter passing over colored the distillate yellow or orange. On adding an excess of sulfuric acid and redistilling into potassium hydroxide solution, organic matter again passed over. This interfered with the silver nitrate titration.

Various studies have been made of the Prussian blue colorimetric method, by Berl and Delpy[4] by Lander and Walden,[5] by Vorländer,[6] by Knight,[7]

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[1] *Proc. Roy. Soc.* (*B*), **82**, 574 (1910).

[2] *The Analyst*, **35**, 471 (1910); **36**, 269 (1911).

[3] Cassava, U. S. Bur. Chem., *Bull.* **106**, 12.

[4] *Ber.*, **43**, 1430 (1910).

[5] *The Analyst*, **36**, 266 (1911).

[6] *Ber.*, **36**, 181 (1913).

[7] *J. Ind. Eng. Chem.*, **6**, 909 (1914).

and by Viehoever and Johns.[1] In this method, the cyanide solution must be concentrated to a very small volume and reagents added proportional to the amount of cyanide present to secure the maximum density of color.

The thiocyanate method of Francis and Connell[2] was investigated. In their method, they add 50 cc. of concentrated sulfuric acid to 50 g. of sample and 200 cc. of water in a liter distilling flask and distil about 150 cc. into 50 cc. of a 4% solution of potassium hydroxide. The distillate is made up to 250 cc. and to an aliquot of 50 cc. is added 1 cc. of yellow ammonium sulfide. The aliquot is evaporated to dryness on the water bath, taken up with 10 to 15 cc. water and barely acidified with hydrochloric acid. The sulfur is filtered off and one-half cc. of dilute hydrochloric acid added. The solution is boiled five minutes and filtered, and the boiling and filtering continued until the solution is absolutely clear. It is then made up nearly to the mark in a 50 cc. Nessler tube and 15 drops of 5% ferric chloride solution is added. The red color is matched with diluted portions of a standard solution containing potassium thiocyanate equivalent to 1 mg. of potassium cyanide per cc.

Discussion of the Francis and Connell Method.—The equilibrium of the reaction between a thiocyanate and ferric chloride is easily disturbed by any factor influencing the ionization of the reacting substances. A few experiments will show the influence of the presence of potassium chloride and of hydrochloric acid. One cc. of the standard thiocyanate solution was made up in Nessler tubes in various concentrations of potassium chloride or of hydrochloric acid, 15 drops of 5% ferric chloride were added, and the color was matched with the standard solution. The results are shown in Table I and by the curves in Fig. 1.

TABLE I.

Influence of Potassium Chloride and Hydrochloric Acid on the Thiocyanate Color.

Conc. HCl.	Color equivalent in cc. of standard.	Conc. HCl.	Color equivalent in cc. of standard.	Conc. HCl.	Color equivalent in cc. of standard.
10%	0.3	5%	0.35	0.1	1.6
5	0.4	4	0.45	0.5	1.7
2	0.45	3	0.55	0.01	1.5
1.3	0.5	2	0.7	0.005	1.4
1.0	0.6	1	0.8	0.001	1.2
0.5	0.7	0.5	1.0	0.0005	1.1
0.1	1.0	0.3	1.3		

The curve in Fig. 1 shows the great influence of the concentration of hydrochloric acid on the thiocyanate color. Small amounts of acid increase the color but increasing quantities of acid decrease the color, as do increasing quantities of potassium chloride. Yet Francis and Connell

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[1] THIS JOURNAL, **37**, 601 (1915).

[2] *Ibid.*, **35**, 1624 (1913).

say to add one-half cc. of dilute hydrochloric acid in excess, not specifying the strength of the acid. They state,[1] "If too much acid is present, the solution will be lemon-yellow. If alkaline, the iron will be precipitated." The solution to be compared with the standard will contain 1.06% potassium chloride and 0.1% of hydrochloric acid, if the one-half cc. of dilute acid added in excess was of 10% strength. One cc. of thiocyanate in these concentrations of acid and potassium chloride matched in color 1.3 cc. of the standard. Francis and Connell state that there is a tendency toward high results in their method and this is probably the cause.

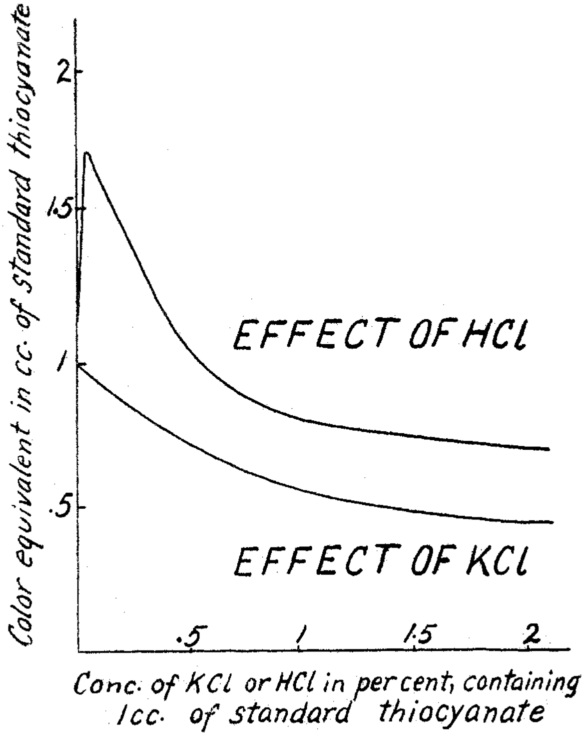

Fig. 1.—Curves showing the effect of potassium chloride and hydrochloric acid on the thiocyanate color.

The influence of temperature on the thiocyanate color was investigated. An increase in temperature increases the color of the thiocyanate alone, but decreases it in the presence of hydrochloric acid and potassium chloride. A difference of five degrees in temperature made little appreciable difference in the color. If solutions to be compared are both at room temperature, the temperature factor should not affect results.

As shown by Viehoever and Johns[2] a volatilization of some of the free thiocyanic acid took place on long boiling but the loss was found to be small. When a solution containing 3 cc. of the standard thiocyanate was boiled vigorously under the condition of the method for ten minutes, less than 0.2 cc. was lost.

Fair results were obtained by the Francis and Connell method by adding to the standard thiocyanate hydrochloric acid and potassium chloride equal to that in the solution to be compared, but the removal of the sulfur

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[1] *Loc. cit.*

[2] This Journal, 37, 601 (1915).

in the method is a tedious process. It is believed that the following method will be found convenient and accurate.

Description of the Method.

Distil the hydrocyanic acid from the sample into potassium hydroxide solution after adding sulfuric acid according to the Francis and Connell[1] method or after enzyme hydrolysis. To 50 cc. of the solution containing 0.1 to 8 mg. of potassium cyanide add 1 cc. of yellow ammonium sulfide and evaporate to dryness on the water bath. To the residue add 10 cc. of acetone and rub with a small glass or porcelain pestle to effect thorough extraction. Pour off the acetone into a small evaporating dish and repeat the extraction twice. Evaporate the combined acetone extracts to dryness on the water bath. Remove the dish and allow to cool to room temperature. Take up the residue in water, make up to 50 cc. in a Nessler tube and add 2 cc. of 0.5% ferric chloride solution. Match the color with standards made by diluting various quantities of a solution containing potassium thiocyanate equivalent to one milligram of potassium cyanide per cc. Mix the ferric chloride well with the solution before comparing. If the distillate is colored by organic matter and also the acetone extract, the following procedure should be adopted:

After evaporating the combined acetone extracts to dryness, take up the residue in 15 cc. of water and pour into a small separatory funnel. Wash the dish with two 5 cc. portions of water, pouring the wash water into the funnel. Add to the funnel 25 cc. of ethyl acetate which has previously been extracted several times with water to remove any soluble impurities. Shake well and allow to settle. The yellow color will be taken up by the ethyl acetate. Drain off the clear water solution into an evaporating dish and evaporate to dryness. Take up in water, make up to 50 cc. in a Nessler tube and compare with standard as usual.

Discussion of the Method.—Potassium thiocyanate is very soluble in acetone, while potassium hydroxide and potassium sulfide will not dissolve. To test the completeness of the acetone extraction, 1 cc. of yellow ammonium sulfide was added to each of two potassium hydroxide solutions containing 8 mg. of potassium cyanide. No. I was evaporated to a thick paste, No. II to dryness. The residues were extracted as in the method with five 10-cc. portions of acetone, but the acetone extracts were evaporated separately to dryness, and the thiocyanate and its potassium cyanide equivalent determined in each. The results are given in Table II.

When the solution is evaporated to a thick paste, the acetone dissolves the thiocyanate slightly better, but much less organic matter is taken up by the acetone when evaporated to dryness. Acetone of technical purity was used with good results.

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[1] This Journal, **35**, 1624 (1913).

TABLE II.

Test of Completeness of the Acetone Extraction.

No. of extract.	Potassium cyanide in mg. in thiocyanate extracted.	
	I.	II.
1	7.5	7.3
2	0.5	0.7
3	Trace	Trace
4	None	None
5	None	None

To test the ethyl acetate extraction, 8 cc. of the standard thiocyanate solution were made up to 25 cc. and extracted with 25 cc. of washed ethyl acetate. The thiocyanate in the water solution was determined as usual and matched in color 8 cc. of the standard. The ethyl acetate was washed with three portions of 25 cc. water and the thiocyanate in each determined. The first portion showed a faint trace, less than 0.1 cc. of the standard, and the second and third showed no thiocyanate present. The yellow color due to organic matter will usually be removed by one extraction with ethyl acetate, but, if not, further extractions will leave the thiocyanate solution colorless. If the ethyl acetate extraction is used, the solution should be matched with the standard soon after adding the ferric chloride, since water extracts of ethyl acetate, after adding ferric chloride, give a yellow color on long standing.

The thiocyanate color is proportional to the amount of ferric chloride added. Since the range of potassium cyanide to be determined lay between 0.1 and 8 milligrams, 2 cc. of 0.5% ferric chloride were added as giving the greatest color change between these limits. The method can be adapted to quantities of cyanide greater or less than these limits by adding less or greater quantities of ferric chloride to the solution and to the standard.

To determine the accuracy of the method as a whole, solutions of about 1% potassium hydroxide were made up and to these were added quantities of a standardized potassium cyanide solution corresponding to 8, 6, 4, 2 and 1 milligrams of potassium cyanide. The potassium cyanide in these solutions was determined according to the method, both with and without the extraction with ethyl acetate, and the results agreed exactly with the theoretical.

A difference in thiocyanate color can be distinguished as follows: 0–4 cc. of standard, 0.1 cc.; 4–8 cc. of standard, 0.2 cc.

Summary.

(1) It has been shown that modifications are necessary in the Francis and Connell[1] thiocyanate method for the determination of small quantities of hydrocyanic acid and a modified method has been indicated.

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[1] THIS JOURNAL, 35, 1624 (1913).

(2) A convenient and accurate method has been given for the determination of small quantities of hydrocyanic acid by the thiocyanate method, the potassium thiocyanate being leached out by means of acetone.

(3) Organic coloring matter can be removed from the thiocyanate solution by extraction with ethyl acetate.

HONOLULU, HAWAII.

THE SOLUBILITIES OF SEVERAL SUBSTANCES IN MIXED NONAQUEOUS SOLUTIONS.

BY J. W. MARDEN AND MARY V. DOVER.

Received January 19, 1916.

Introductory and Historical.—It is pretty generally agreed that the solubility of materials in mixed solvents is not as great as in one or other of the pure solvents. Mixtures of nonaqueous liquids are not infrequently recommended, however, for solution and separation. For example, the United States Pharmacopeia suggests the use of ether-chloroform for the extraction of quinine. Thorpe[1] suggests its extraction by means of a benzene-chloroform solution. In some cases the second solvent is used for the purpose of excluding undesirable materials. This can scarcely always be the case.

The solubilities of a number of substances have been determined in mixed aqueous solutions and a number of irregularities noted. The solubility of acetanilide,[2] for instance, has been shown to be greatest in 90% ethyl alcohol at 25°. If the concentration of the alcohol is either increased or decreased, the solubility is lowered. According to Müller,[3] the solubility of strychnine at 20° in water is 0.021 g. strychnine per 100 g., while in ether it is 0.0342 g. In water saturated with ether the solubility is 0.0166 g., which value is lower than in either solvent.

Dunkelski[4] has determined the solubilities of certain mercuric salts in given mixed nonaqueous solvents at different temperatures in an effort to show that chemical combination takes place between the solvent and solute in molecular proportions, much as we have the formation of hydrates in aqueous solution.

Bruner[5] has determined the solubilities of iodine in various mixed solutions of nonaqueous solvents. Bruner's work shows that the solubility of iodine is less than proportional to the percentage composition of the solvent. The curves given in his paper are not smooth, but there are no very sharp breaks which might indicate the presence of various solution

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[1] "Dictionary of Applied Chemistry," Vol. V, p. 677, Longmans, Green & Co., New York.

[2] Holleman and Antusch, *Rec. trav. chim.*, **13**, 293 (1894).

[3] *Apoth. Ztg.*, **18**, 258 (1903).

[4] *Z. anorg. Chem.*, **53**, 327 (1907).

[5] *Z. physik. Chem.*, **26**, 145 (1898).