

about 130° with apparent loss of aniline and the formation of $An \cdot HgCl_2$, which then melts at 188°. In the preparation of the more complex types, the constituents were best dissolved in the minimum amount of solvent at room temperature and cooled in a freezing mixture.

Summary

Aniline exhibits a wide capacity to form compounds in combination with halogen and different metals. Seventeen types, including hydrated forms, are recognized. No correlation with properties can be made of all of these compounds on the basis of modern theories. The octo-aniline compound of mercury is easily prepared and is of special interest.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF CYANIDE IN SMALL AMOUNTS

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RECEIVED AUGUST 10, 1928

PUBLISHED APRIL 5, 1929

The following method is the application of an established reaction in organic chemistry for the quantitative estimation of cyanide in small amounts. The method depends on the development of a reddish-brown color due to the formation of the sodium or potassium salt of isopurpuric acid, which occurs when cyanide is added to an alkaline picrate solution. In the presence of an excess of alkaline picrate the development of the color is quantitative, making it possible to estimate the amount of cyanide present colorimetrically by comparison with a standard prepared with a known amount of cyanide.

Durien² applied such a method for the quantitative estimation of hydrocyanic acid in bitter almond water. Runne,³ in a survey of the quantitative methods for the determination of cyanide, established the procedure of Durien as accurate to within one per cent. Waller⁴ used a similar method in the analysis of tissue distillates for hydrocyanic acid. From a stock solution of alkaline picrate containing a definite amount of cyanide, color standards are prepared with which the unknown solution is compared. Furthermore, as Waller has pointed out, the reaction has been described previously as a qualitative test for cyanide, by various workers.⁵

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² Durien, *Jahresb. Pharm.*, **37**, 439 (1902).

³ Runne, *Apoth.-Ztg.*, **24**, 357 (1909).

⁴ Waller, *J. Physiol.*, **40** (Proceedings of the Physiological Society, June 18) (1910).

⁵ Hlasiwetz, *Ann.*, **110**, 289 (1859); Reichardt, *Chem.-Ztg.*, **25**, 537 (1901); Guignard, *Ann. sci. pharmacol.*, 415 (1906).

However, since the method has been developed in a somewhat different manner and as some of its possibilities and limitations have been examined, it is considered to be of sufficient interest to report.

The details of the method which have been found to give satisfactory results are as follows. Into a test-tube with a 25-cc. graduation are pipetted 3 cc. of saturated picric acid solution, 1 cc. of 5% sodium carbonate solution (which ensures an alkaline reaction) and 1 cc. of the cyanide solution to be determined. The tube is heated in a boiling water-bath for five minutes, then cooled in running water and the volume made up to 25 cc. The solution is then compared in a colorimeter with a standard prepared in an identical manner. The amount of cyanide which has been found satisfactory for the standard is 1 cc. of *N*/500 potassium or sodium cyanide, a depth of solution of 20 mm. being used in the colorimeter.

Using such a procedure Table I shows the results of a series of determinations of solutions of sodium cyanide of various concentrations. All solutions were prepared from the same stock solution (*N*/10 sodium cyanide) to avoid errors due to standardization. The results demonstrate the determination of sodium cyanide in amounts of the order of 0.1 mg. within 1% error.

TABLE I

QUANTITATIVE DETERMINATION OF SODIUM CYANIDE SOLUTIONS							
Standard contained 1 cc. of <i>N</i> /500 sodium cyanide soln. (0.0980 mg. of NaCN)							
1 cc. of <i>N</i> /600 soln. (0.0817 mg. of NaCN)		1 cc. of <i>N</i> /550 soln. (0.0891 mg. of NaCN)		1 cc. of <i>N</i> /450 soln. (0.1088 mg. of NaCN)		1 cc. of <i>N</i> /400 soln. (0.1225 mg. of NaCN)	
Col. reading, mm.	Amt. dctd., mg.	Col. reading, mm.	Amt. dctd., mg.	Col. reading, mm.	Amt. dctd., mg.	Col. reading, mm.	Amt. dctd., mg.
24.1	0.0813	22.1	0.0887	18.0	0.1088	15.9	0.1233
23.9	.0820	22.0	.0891	18.0	.1088	16.1	.1217
24.0	.0817	22.0	.0891	18.2	.1077	15.9	.1233
24.0	.0817	22.2	.0883	17.9	.1094	15.9	.1233
24.0	.0817	22.2	.0883	18.2	.1077	16.0	.1225

In the boiling water-bath the color develops rapidly, about 90% of the intensity being present in two minutes. It gradually increases up to five or six minutes' heating and then fades slightly on further heating. After ten minutes in the water-bath there is a slight but definite decrease in the intensity and after twenty minutes this decrease amounts to approximately 5%. On heating for one hour the decrease in intensity approaches 20%.

Although the color developed by heating on a water-bath for five minutes is approximately 90% of the intensity obtained by boiling to a small volume over an open flame, it has been arbitrarily adopted in the method as the procedure is more convenient, especially if a number of determinations are to be made. Moreover, it is permissible in that constant results are given. At room temperature the color becomes apparent within one minute after the addition of the cyanide to the alkaline picrate solution. It develops comparatively rapidly at first, reaching 50% of its intensity in from one-half to one hour after the addition of the cyanide. It attains its maximum only after standing from twenty-four to forty-eight hours.

The color developed has been found to be permanent for at least one month.

A consideration which is of importance is the fact that a picric acid solution alkalinized with sodium hydroxide yields a reddish-brown color even in the absence of cyanide, the intensity of the color varying with the concentration of the alkali. Moreover, the intensity of the color de-

veloped by cyanide is decreased in the presence of sodium hydroxide. This appears to be rather a serious obstacle in that cyanide distillates are commonly collected in a solution of sodium or potassium hydroxide. However, such solutions neutralized with hydrochloric acid yield accurate results, so the difficulty may be obviated in this manner. In the presence of an appreciable quantity of the potassium ion there is a precipitation of potassium picrate due to the low solubility of that salt. However, on heating it is redissolved and remains in solution on diluting to the 25-cc. volume.

In the application of the method it must be remembered that the presence of certain reducing substances which cause the formation of a reddish color in alkaline picrate solutions will interfere with the validity of the test. Among these are sulfides, hydrosulfites, aldehydes and ketones, including the reducing sugars. However, these substances must be present in a concentration of a much higher order than that of cyanide before they become a factor. A number of compounds have been tested with a view to gaining some idea of this relationship. Table II shows the concentrations of the various substances necessary to produce a color of an intensity comparable with that of the standard when 1 cc. of the solution is used in the test according to the above procedure. It is evident from these results that in order to be a factor such substances must be present in very appreciable quantities. The possibility of obtaining furfural or its derivatives in tissue distillates was considered. On boiling liver and muscle tissue in 2% tartaric acid solution, a qualitative alkaline picrate test on the distillate was negative. In order to subject to a more crucial test the possibility of the formation of furfural compounds by the action of tartaric acid on carbohydrates, the following experiment was made. Gum arabic, a pentose which is more readily decomposed by acids than are hexoses, was boiled in 10% tartaric acid, a concentration much greater than that necessary for distilling cyanide from tissues.⁶ The distillate gave a negative alkaline picrate test and a very faintly positive Molisch test. Consequently it was concluded that furfural compounds would not be an interfering factor in tissue distillates.

TABLE II

RESULTS OF TESTS			
Substance	% ^a	Substance	% ^a
Standard (potassium cyanide)	0.011	Formaldehyde (40%)	} Color too pale to compare
Ammonium sulfide	0.4	Acetoacetic ester	
Dextrose	0.4	Ethyl acetate	} No color developed
Acetaldehyde	15.0	Ethyl alcohol	
Acetone	20.0	Methyl alcohol	
Furfural	10-15	Acetic acid	

^a Percentage of substance necessary to give color comparable with the standard.

⁶ Bischoff, *Ber.*, 16, 1351 (1883).

Used qualitatively the test is very sensitive. By looking through the depth of a test-tube of solution against a white background and comparing with a control tube of alkaline picrate solution, the detection of very small amounts of cyanide is made possible. In the 25-cc. volume used in the test one in ten million (CN) is very easily distinguished, one in twenty million (CN) is quite distinct and one in fifty million is distinguished definitely but with more difficulty.

I wish to thank Dr. A. L. Tatum for the suggestion and direction of this research.

Summary

1. A method for the quantitative determination of cyanide in amounts of the order of 0.1 mg. within 1% error is described. The method depends on the formation of a reddish-brown color which occurs when cyanide is added to an alkaline picrate solution.

2. The effects of time and temperature on the development of the color are discussed.

3. The presence of certain reducing substances which cause the development of a red color in alkaline picrate solutions may invalidate the method. The concentration of such substances necessary to be an interfering factor is indicated.

4. Used qualitatively the test is sensitive to one part of cyanide (CN) in fifty million.

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THE FORMATION OF PYRROLINES FROM GAMMA-CHLOROPROPYL AND CYCLOPROPYL KETIMINES¹

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RECEIVED AUGUST 24, 1928

PUBLISHED APRIL 5, 1929

In a long, interesting paper appearing in 1923 de Booseré² reported the isolation of ethyl cyclopropyl ketimine and its hydrochloride with several other products following the action of magnesium ethyl bromide on γ -chlorobutyronitrile. The mechanism indicated by him for the origin of the ketimine follows closely an earlier one formulated by Bruylants³ for an entirely analogous reaction. The equations follow.

¹ This paper is constructed from the first part of a dissertation to be presented by John B. Cloke to the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² De Booseré, *Bull. soc. chim. belg.*, **32**, 26-51 (1923).

³ Bruylants, *Bull. sci. acad. roy. belg.*, **12**, 1082-1084 (1908).