3. The mixture should stand about one or two hours to give the best yields, although good yields may be obtained in fifteen to thirty minutes.

The results of these experiments show that lead selenate is the better material to use because it gives a better yield and requires less ammonium carbonate and less time than does the barium selenate.

Increase of temperature, stirring with a current of air or carbon dioxide, or carrying out the reaction in sealed tubes does not increase the yield.

UNIVERSITY OF INDIANA.
BLOOMINGTON, IND.

[CONTRIBUTION OF THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION.]

A MODIFICATION OF THE DIPHENYLAMINE TEST FOR NITROUS AND NITRIC ACIDS.

BY W. A. WITHERS AND B. J. RAY

Received February 28, 1911.

Diphenylamine was discovered by Hofmann[1] in 1864, and the blue coloration which he found that it gives with various oxidizing agents has since been used for the detection of the presence of minute amounts of nitric acid.

In 1872 Kopp[2] first proposed its use for the detection of nitrous acid in commercial sulfuric acid.

In 1875 Böttger[3] proposed that the reaction of Kopp be used for the detection of the presence of nitrites and nitrates in potable waters.

Since that time various chemists have given consideration to the subject and have proposed modifications of the methods of applying the test—some of them being very delicate and others less so. It was the need of a reliable and delicate test for nitrites and nitrates which led us to take up this work.

For preparing the reagent Cohn[4] and Wiley[5] use diphenylamine and concentrated sulfuric acid and specify no relation between the amounts except that Wiley refers to 4 cc. of sulfuric acid. Fresenius[6] and Eggermainz[7] use 10 mg. and Muller[8] 20 mg. of diphenylamine to 100 cc. of concentrated sulfuric acid. Warrington[9] dissolves in an indefinit amount of water and adds an indefinit amount of concentrated sulfuric acid. Lunge[10] and Treadwell[11] use 500 mg. of diphenylamine for each 100 cc. of concentrated sulfuric acid and add 20 cc. of water. Hager[12] uses 1 gram to each 150 cc. of acid, and adds 30 cc. of alcohol, and Cimmino[13] uses 5 per cent. of hydrochloric acid without giving the relation between the diphenylamine and sulfuric acid.

The manner of making the test differs with different chemists. To 1 cc. of the liquid to be tested, the amount of diphenylamine reagent to be used is specified as "1 drop," "3 to 4 drops," "a few drops" and "5 cc.," and in some instances no amounts are stated. Some use also sul-

furic acid in making the test. Some float the liquid to be tested upon the reagent, some mix the liquid and reagent and float the mixture over concentrated sulfuric acid, and Wiley[5] heats at 80 degrees for 15 minutes. Some simply say "treat" and give no details. The table given below shows these facts more in detail.

The manner of making the test is of considerable importance. When the amount of nitrate or nitrite is small it is possible to place the two liquids in layers without the development of a color. In this case the color will develop promptly upon gentle agitation which causes a slight mixing of the liquids at the plane of contact. This blue band may be made to disappear entirely upon thoroughly mixing the liquids if the nitrates and nitrites are in small amounts.

An excess of diphenylamine over the amount required for the reaction actually retards or prevents the development of the coloration. This was shown by us in a series of tests in which varying amounts of the diphenylamine reagent were used. When we used one, two or three drops of the Treadwell[11] reagent, 2 cc. of the liquid to be tested and 2 cc. of concentrated sulfuric acid we obtained a good ring, but when we used five, seven or ten drops of the same reagent and other conditions as before no satisfactory coloration was developed.

The amount of sulfuric acid is extremely important and the addition to it of small amounts of a mixture of diphenylamine reagent and nitrate-bearing liquid which have not given the test will frequently develop a strong coloration.

Warrington in 1885 referred to the greater delicacy of the test in the presence of chlorides and in 1889 Cimmino proposed the use of 5 per cent. hydrochloric acid either by adding a few drops of this acid in making the test or by adding this acid to the solution of the base in sulfuric acid. In a test tube he placed 1 cc. of the solution to be tested, 3 or 4 drops of the diphenylamine solution in sulfuric and hydrochloric acids, 2 cc. of concentrated sulfuric acid and shook. In any case the color develops gradually and reaches the maximum after some minutes; an elevated temperature hastens the development of the color. Practically any of the methods will show the presence of one part of nitrate nitrogen in 10 million.

Combining some of the features of the different methods we have prepared a reagent which in our hands has proven to be very delicate. It is made in the following manner: 700 mg. of diphenylamine are dissolved in a mixture of 60 cc. of concentrated sulfuric acid and 28.8 cc. of distilled water. The resulting mixture is thoroughly cooled and 11.3 cc. of concentrated hydrochloric acid (sp. gr. 1.19) are added slowly, making the hydrochloric acid content 5 per cent. After standing over night some of the base separates, showing that the reagent is saturated. The

Chemist.	Reagent. Diphenylamine.	Reagent. H_2SO_4.	Reagent. H_2O	Reagent. Other substances	Amount of reagent used.	Amount of unknown used.	H_2SO_4 used.	Temperature.	Time.	Procedure.	Delicacy claimed. 1 part of nitrogen to
Treadwell[11]	500 mg.	100 cc.	20 cc.	..	..	..	..	..	..	Float liquid to be tested on the reagent.	
Cohn[4]	..	..	..	..	few drops	1 cc.	1 cc.	..	..	Mix liquid and reagents, float on H_2SO_4.	13,000,000
Wiley[5]	..	4 cc.	..	..	1 drop	1 cc.	..	80° C.	15 min.	Add 1 drop of reagent to liquid. Keep at 80° for 15 min.	
Fresenius[6]	1 mg.	10 cc.	..	..	few drops	..	..	..	..	Float reagent and liquid over H_2SO_4.	
Hager[12]	1 gram	150 cc.	..	30 cc. alcohol	..	..	..	..	..	Float liquid on reagent.	20,000
Warrington[9]	..	..	..	..	2 drops	2 cc.	5 cc.	..	..	"Treat."	10,000,000
Muller[8]	200 mg.	1 liter	..	..	5 cc.	1 cc.	..	..	..	Treat 5 cc. of reagent with 1 cc. of unknown.	7,700,000
Eggermainz[7]	0.01 gram	100 cc.	..	..	10 cc.	Several cc.	..	..	20 min.	"Treat"	44,200,000
Cimmino[13]	..	..	..	5% HCl	3–4 drops	1 cc.	2 cc.	..	..	Treat and shake.	1,000,000
Withers and Ray	700 mg.	60 cc.	28.8 cc.	11.3 cc. HCl (1.19)	1 drop	1 cc.	2 cc.	40° C.	15 min.	Float liquid and reagent over H_2SO_4, agitate gently. Place in bath at 40° C. for 15 min.	35,000,000
Withers and Ray	700 mg.	60 cc.	28.8 cc.	11.3 cc. HCl (1.19)	1 drop	1 cc.	2 cc.	40° C.	1 hour	Float liquid and reagent over H_2SO_4, agitate gently. Place in bath at 40° for 1 hour.	44,200,000

test with the diphenylamine reagent as prepared by us is conducted as follows: Place 1 cc. of the liquid to be tested in a clean test tube; add 1 drop of the diphenylamine reagent and mix thoroughly by shaking. From a pipe is added 2 cc. of concentrated sulfuric acid, while the tube is held at an angle so as to form two layers of the liquids. The tube is gently agitated so as to cause a slight mixing of the liquids at the plane of contact, and it is then placed in a bath at the temperature of 40° and left for 15 or 20 minutes. This method will reveal the presence of one part of nitrite nitrogen in 25 million or one part of nitrate nitrogen in 35 million. By heating for one hour instead of 15 or 20 minutes the test will show one part of nitrite nitrogen in 32 million or one part of nitrate nitrogen in 44 million.

REFERENCES.

[1] *Ann.* **132**, 160.
[2] *Ber.*, **5**, 284.
[3] *Jahresb. Tier-Chem.*, **1875**, 918.
[4] "Indicators and Test Papers," **1907**, p. 68.
[5] "Principles and Practice of Agricultural Analysis," I, p. 532.
[6] "Qual. Anal"., Trans., **1906**, p. 388.
[7] *Bull. soc. chim.*, **1889**, 350.
[8] *Bull. soc. chim.*, **1889**, 670.
[9] *Chem. News*, **51**, 41.
[10] *Z. angew. Chem.*, **1894**, 345.
[11] Treadwell-Hall, "Analytical Chemistry," **1907**, I, p. 340.
[12] *J. Chem. Soc. Abs.*, **50**, 99 (1886).
[13] *Z. anal. Chem.*, **39**, 429 (1899).

WEST RALEIGH, N. C.

PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS CONTAINING AMMONIA AND CITRIC ACID.

BY ROBERT A. HALL AND JAMES M. BELL.

Received February 22, 1911.

In the analysis of commercial fertilizers for the so-called "available" phosphoric acid, it is usual to employ a solution of "exactly neutral" ammonium citrate,[1] having a specific gravity of 1.09 at 20°. After extraction of the fertilizer with water, the residue is treated with the citrate solution and the phosphoric acid which remains undissolved is termed insoluble, or non-available; that which the water dissolves is the water-soluble; and that dissolved in the citrate solution is the reverted or citrate-soluble. The sum of the water-soluble and the citrate-soluble phosphoric acid constitutes the available. Upon the results of these analyses depend the valuation of the fertilizer material, and, if the guarantee accompanying the fertilizer claims a higher percentage of phosphoric acid than is shown in the analysis by the state chemist, the manufacturer is liable to a fine.

[1] Bureau of Chemistry, *Bull.* 107 (revised), 1.