cannot be exceeded without obtaining a dark and loosely adherent deposit) rapidly becomes less as the silver content of the solution becomes less. When the amperage had become practically zero, the voltage was allowed to rise gradually to 1.3–1.4 volts and electrolysis continued until a total of 25–30 minutes had elapsed. This period must necessarily be larger if the quantity of silver to be deposited is greater than that which we used.

Then, without disturbing the apparatus, about 3 g. of oxalic acid crystals were added to the solution, and enough concentrated hydrochloric acid to make the solution faintly acid to litmus paper. Without increasing the applied voltage, electrolysis was continued for about 20 minutes. Then the experiment was terminated, and the electrodes were washed and dried in the manner described in the preceding paper. The following results were obtained:

TABLE I.—DEPOSITION OF SILVER.

Silver present.	Found.	Error.	
G.	G.	G.	%.
0.1595	0.1591	—0.0004	—0.25
0.5887	0.5886	—0.0001	—0.02
0.3704	0.3699	0.0005	—0.14
0.2958	0.2956	0.0002	—0.07
0.4030	0.4027	0.0003	—0.07
0.5139	0.5139	0.0000	0.0
0.2551	0.2551	0.0000	0.0

AUSTIN, TEXAS.

[CONTRIBUTION FROM THE DEPARTMENT OF SOIL BIOLOGY OF THE OHIO AGRICULTURAL EXPERIMENT STATION.]

TITRAMETRIC DETERMINATION OF NITRITES.

BY B. S. DAVISSON.

Received May 10, 1916.

The frequent necessity of determining nitrites in the investigation of the physiology of the process of nitrification, reveals the need of a satisfactory titrametric method for such determination.

Nitrite determinations are usually made by colorimetric methods. It would be more desirous to make nitrite determinations titrametrically and avoid the errors which are so often introduced in colorimetric methods, namely, errors of dilution, eye fatigue, color comparison and the individual error of the worker.

Historical.

The reaction of nitrous acid with hydriodic acid is well known: $2HI + 2HNO_2 \longrightarrow 2H_2O + 2NO + I_2$. Since this reaction proceeds quantitatively, titration of the liberated iodine with standard thiosulfate has been used as a titrametric method for determining nitrous nitrogen. The nitric oxide evolved in the reaction passes readily back into nitrous acid in contact with air and water and will oxidize more hydriodic acid, unless air is excluded from the titrating flask.

Winkler[1] has worked out a time method for determining small amounts, less than $^1/_3$ mg., of nitrites in waters. The method depends upon the reactions taking place in the presence of oxygen. After the solution has stood for some time in contact with the acid, iodide and starch solution, the liberated iodine is titrated with 0.005 N sodium thiosulfate. The author compiled a table showing the milligrams of N_2O_3 in a liter of the solution for a given quantity of the thiosulfate. The table is compiled for periods of 3, 6 and 24 hours. The author recommends the 24-hour period as giving the most satisfactory results.

Winkler[2] proposed a second method for determining nitrites when the quantity present is greater than $^1/_3$ mg. N_2O_3. He used $KHCO_3$ as a source of CO_2 to expel the air from the titration flask. After ten minutes the iodine is titrated.

Sutton[3] outlines the Dustan and Dymond method in which the air is expelled from the flask by boiling the solution of acid, starch and potassium iodide and closing off the flask with a pinchcock, thus creating a vacuum when the solution cools. The nitrite solution is then introduced and the liberated iodine titrated with standard thiosulfate.

Wiley[4] outlines the Chabier method for the quantitative determination of nitrites. The air is expelled from the titrating flask by carbon dioxide or illuminating gas. The reaction of the acid, potassium iodide, and starch solution is allowed to take place after the air is expelled, and the liberated iodine is titrated with standard thiosulfate.

Experimental.

The two methods proposed by Winkler were investigated. The procedure was the same as that employed by Winkler.

The results obtained by the first method were too high in practically all of the determinations made. No satisfactory results were obtained from a great number of trials.

Since this method depends upon the reaction taking place in the presence of oxygen, it seems probable that one might pass a slow current of air through the solution and accomplish the desired oxidation in a very short time. This, of course, would require the formulation of another table to be used in connection with the method.

Winkler's second method gave no better results than those obtained by his time method. Trouble was experienced in getting all the oxygen out

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[1] *Z. Nahrungs und Genussmittel,* 29 (1915).

[2] *Loc. cit.*

[3] "Volumetric Analysis," 10th Ed., p. 287.

[4] "Princip. and Pract. of Agric. Analysis," 2nd Ed., Vol. II, p. 474.

of the flask. Five grams of $KHCO_3$ as recommended by Winkler, was not sufficient. It is necessary that no air enter the flask during titration and this can be accomplished only when a rapid current of CO_2 passes out of the solution. The results obtained with this method were in every case too high.

The work was carried no further on the method proposed by Winkler. The method cannot be used where large quantities of nitrites are present. Since the amount of nitrite which we wish to determine may be large or very small, it was thought better to develop a method which can be used with both large and small quantities of nitrites.

The Dustan and Dymond method was next used. Special burets were prepared for the standard thiosulfate and nitrite solutions. The burets were connected with the flask through a two-way stopcock and all air was excluded in making the connections. It was found almost impossible to prevent the leakage of air into the flasks. Air was drawn in about the rubber stoppers, though they appeared to be very tight. A method simpler in manipulation and still capable of a high degree of accuracy was sought.

Since the iodometric method of determining nitrite nitrogen depends upon the determinations being carried on in the absence of oxygen, it would be better to expel the air by means of some inactive gas and make the titrations while a slow current of this gas is passing through the flask. The Chabier method with some improvements should give trustworthy results for fractions of a milligram. The starch iodide reaction is extremely delicate and if careful precautions are taken to expel all air one should get excellent results.

Either natural gas or commercial carbon dioxide may be used to expel the air from the titration flask. These gases were each found to be effective. The low cost and ease of handling of carbon dioxide makes it easily available for this purpose and it is used in this laboratory. It requires no further purification and can be passed directly from the cylinder through the flask.

A special aeration flask was used, as shown in Fig. 1. It is a large-mouthed Erlenmeyer flask with an aerating tube sealed through the side and extending to the bottom of the flask where an arm is bent parallel to the flask bottom. The tube has several openings on either side to permit a rapid escape of gas. Such an arrangement gives good distribution of the gas and enables one to get immediate expulsion of the air. The flask is closed with a rubber stopper bearing an outlet for the gas, a separatory funnel for introducing the acid, a buret for the standard thiosulfate and a second

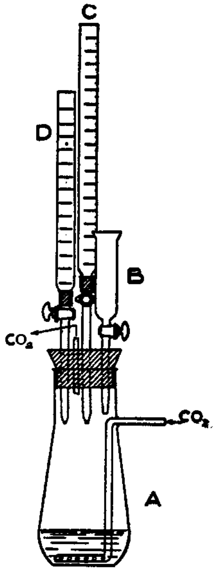

Fig. 1.

buret to carry a standard nitrite solution to be used in case the end point is overstepped. A stand with a white porcelain base is used with the apparatus.

Procedure.—Bring the solution to be tested into flask A and make to a volume of about 150 cc. Add 0.5 g. of pure KI and 2 cc. of a starch solution. Insert the stopper and allow a slow current of CO_2 to pass through the flask for three minutes. Reduce the current of CO_2 to a few bubbles, just sufficient to prevent any diffusion of air into the flask during titration. Add about 10 cc. of a 15% solution of H_2SO_4, and allow the solution to react for a short time before titrating the liberated iodine with thiosulfate.

The results reported in this paper were obtained upon a standard nitrite solution. The nitrite solution was prepared from silver nitrite, the silver being precipitated from the solution with sodium chloride. The solution was filtered, the precipitate washed free of nitrites and the solution then made to a definite volume. Standard thiosulfate of 0.1 *N*, 0.05 *N*, 0.02 *N* and 0.005 *N* strengths were used for making titrations.

Table I contains results obtained where variable quantities of a standard nitrite solution were used. Twentieth normal thiosulfate was used in making the titrations.

TABLE I.

Nitrite solution. Cc.	$Na_2S_2O_3$. Cc.	Nitrogen taken. Mg.	Nitrogen found. Mg.	Error.
25.06	12.07	8.51	8.47	−0.04
22.86	11.05	7.77	7.74	−0.03
25.35	12.22	8.61	8.56	+0.05
22.84	11.05	7.76	7.74	−0.02
18.20	8.86	6.18	6.20	+0.02
18.05	8.85	6.13	6.19	+0.06
17.93	8.71	6.09	6.10	+0.01
18.59	9.03	6.32	6.33	+0.01
20.28	9.90	6.89	6.93	+0.04

Two series were carried out with solutions containing 15.1 and 2.01 mg. of nitrogen as nitrite, respectively.

TABLE II.

No.	Cc. 0.1 *N* $Na_2S_2O_3$.	Nitrogen. Mg.	Cc. 0.02 *N* $Na_2S_2O_3$.	Nitrogen. Mg.
1	10.77	15.08	7.35	2.06
2	10.82	15.14	7.26	2.03
3	10.86	15.20	7.26	2.03
4	10.86	15.20	7.20	2.01
5	10.77	15.08	7.17	2.00
6	10.82	15.14	7.08	1.98
7	10.74	15.03	7.26	2.03
Theoretical	...	15.10	..	2.01

The method should give accurate results in the presence of organic matter if it is to be used in the study of the physiology of nitrification.

The effect of organic matter was next studied. Determinations were made in the presence of soil extract which contained considerable organic matter. Fifty cc. of a standard nitrite solution were added to 50 cc. of a soil extract and the nitrite was determined. Nitrites were determined separately on 50-cc. portions of the soil extract and the proper correction, 0.448 mg., was made.

TABLE III.—EFFECT OF ORGANIC MATTER ON NITRITE DETERMINATION. AMOUNT TAKEN, 10 MG. OF NITROGEN.

Cc. 0.1 *N* $Na_2S_2O_3$.	Nitrogen found. Mg.	Nitrogen recovered. Mg.	Cc. 0.1 *N* $Na_2S_2O_3$.	Nitrogen found. Mg.	Nitrogen recovered. Mg.
7.46	10.45	10.00	7.46	10.45	10.00
7.47	10.46	10.02	7.50	10.50	10.05
7.48	10.47	10.03	7.50	10.50	10.05
7.48	10.47	10.03	7.47	10.46	10.00

The organic matter of the extract does not affect the results very materially. In extreme conditions, however, the nitrites may be removed from a second sample by boiling with acetic acid, and the magnitude of the action due to organic matter determined by means of a blank titration.

Small quantities of nitrites may be determined in the open flask while a current of CO_2 is passing through the solution. Table III contains the results of such determinations. For very small quantities of nitrites 0.005 *N* thiosulfate is used.

TABLE IV.—AMOUNT TAKEN, 0.012 MG. NITROGEN.

Cc. 0.005 *N* $Na_2S_2O_3$.	Mg. nitrogen.	Cc. 0.005 *N* $Na_2S_2O_3$.	Mg. nitrogen.
0.19	0.013	0.18	0.012
0.16	0.011	0.17	0.012
0.14	0.009	0.18	0.012
0.19	0.013	0.16	0.011
0.19	0.013		

The results reported in this paper show clearly that nitrous nitrogen can be determined titrametrically when care is taken to expel the air from the titration flask with some gas which will not affect the determination.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY.]

SODIUM PYROGALLATE AS A REAGENT FOR THE DETERMINATION OF OXYGEN.

BY J. W. SHIPLEY.

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TOPICAL OUTLINE.—Introduction and Historical. Reagents. Apparatus. Range of Concentrations. Specific Absorption of Reagents. Comparison with Potassium Pyrogallate. Volume of Oxygen Absorbed before Rate of Absorption Dropped to Four-minute Limit. Rate of Absorption. Temperature Coefficient. Relation of