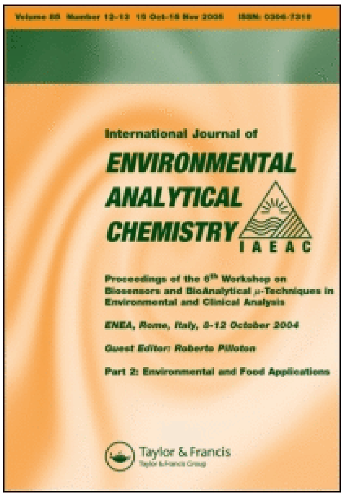

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Spectrophotometric Determination of Nitrate Ion in Fresh Water[†]

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R. S. Lambert and R. J. DuBois (Anal. Chem., 43, 955, 1971) reported a method for the determination of nitrate ion in the concentration range of 1.5 to 9.0 mcg/l in saline waters. In this method, the nitrate ion is reduced to a nitrite ion and a diazo coupling is made to form a species for suitable spectrophotometric determinations in 5-cm cells. This method has been adapted for use on fresh-water samples with nitrate ion levels ranging down to 10 mcg/l. The concentrations of reagents, and the volume of the sample have been changed. These changes, with the use of both 10-cm and 5-cm cells, have provided excellent results over a range of 10 to 5000 mcg/l. The method was quite successful for routine analysis in view of its facility of use and precision provided.

Lambert and DuBois[1] have shown the spectrophotometric determination of nitrate by reduction to nitrite and subsequent diazotization and coupling reactions to be a sensitive test. This sensitivity gives it some advantages over more direct methods such as the u.v. absorption of nitrates in 5% perchloric acid solution and in hydroxide solutions.[2] Phenoldisulfonic acid, brucine, and chromotropic acid are other reagents used for spectrophotometric nitrate determinations, but interferences and exacting conditions for good reproducibility make them somewhat difficult to use.

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The reduction of nitrate to nitrite has been reported using cadmium or zinc as a reducing agent.[2] Similarly, a method using copperized cadmium has also been described.[3] Both zinc and cadmium, however, require careful control of conditions and copperized cadmium proved difficult to produce in the correct ratio of copper to cadmium. A method solving most of these problems was described by Lambert and DuBois[1] for the spectrophotometric determination of nitrate in the presence of chloride. Copper(II) sulfate, ammonium chloride, and dibasic sodium phosphate were used as a mixed catalyst with powdered cadmium to determine nitrate ion concentrations of 1.5 to 9.0 ppm in saline waters. A detection limit of 0.05 ppm was determined, and the method was reported to be suitable for samples containing no chloride.

This method has been adapted, with several modifications, to the analysis of environmental fresh-water samples for a wide range of nitrate concentrations. Good accuracy and precision were obtained over the range from 30 ppb to 5 ppm.

EXPERIMENTAL

Apparatus

A Beckman Model D.U. Spectrophotometer was used for absorbance measurements in conjunction with 5- and 10-cm cells.

Preparation of reagents

The mixed acid reagent was prepared by dissolving the following in sufficient distilled-deionized water to produce 1 l: 40 g of citric acid, 180 g of ammonium chloride, 2.67 g of anhydrous dibasic sodium phosphate, 180 g of sodium chloride, 0.373 g of anhydrous copper(II) sulfate, and 20 ml of acetic acid. This solution is quite close to the saturation point and should be stored in an area where the temperature remains at 20 C° or above to prevent salting out.

The color-developing reagent was prepared by grinding together in a large mortar 30 g of ammonium chloride, 6.72 g of sodium citrate, 2.02 g of manganese(II) sulfate monohydrate, 0.6 g of cadmium powder, and 0.4 g of sulfanilic acid. This mixture was ground until it was homogeneous and completely powdered. Then 0.2 g of l-naphthylamine was added, and grinding continued until the mixture was again homogeneous. This reagent should be stored in a tightly capped vial covered with aluminum foil to keep out light. Since moisture causes deterioration of this reagent, the grinding process should, if possible, be carried out in a low-humidity environment.

Standard nitrate solutions were prepared from potassium nitrate to contain 30, 60, 120, 180, 300, and 420 ppb nitrate ion. These standards comprise series 1. For series 2, standard solutions were prepared to contain 0.5, 1.0, 1.5, 2.0, 3.0, and 5.0 ppm nitrate ion.

Environmental samples were prepared by filtering through Whatman #44 filter paper using a Millipore filtering apparatus.

Recommended procedure

Pipet 25 ml of mixed acid reagent into a 125-ml Erlenmeyer flask and add 25 ml of sample. Mix the solution well, and then add 2.000 ± 0.005 g of color-developing reagent. Stopper and mix by swirling vigorously for at least 30 sec. Let the solution stand for 30 min, then measure the absorbance at 527.5 nm in a spectrophotometer. Read against a distilled-deionized water blank.

Prepare a calibration curve using the above procedure on the six standard nitrate solutions from the desired series.

For samples in the range of series 1, absorbance should be measured with 10-cm cells, whereas for the ppm series, 5-cm cells are preferable.

RESULTS AND DISCUSSION

Table I shows a comparison of concentrations for the various reagents between Lambert and DuBois' original work and this paper. Citric acid remains essentially the same although some difference is noted in the total determination column due to volume difference in sample size and use of a decreased volume of mixed acid reagent. Ammonium chloride was maintained at the same level in the total determination, but was redistributed between the mixed acid reagent and the color-developing reagent. Dibasic sodium phosphate concentration was maintained at the same level as used by Lambert and DuBois in the mixed acid. Sodium chloride concentration was increased for the total determination to bring the concentration to a point where a minimum effect on absorbance would be noted. Since fresh-water samples contain relatively small amounts of sodium chloride as compared to the saline water used in the original work, this addition was necessary to ensure good precision. These levels were determined with the use of the graph from Lambert and DuBois.[1] Increasing the amount of copper(II) sulfate seemed to increase the solubilities of the chlorides, and so produced a more stable mixed acid solution. Total determination acetic acid decreased since it was maintained at the same concentration in the mixed acid.

The color-developing reagent remained essentially the same with the exception, as noted earlier, of an increased ammonium chloride. Total determination concentrations of sodium citrate, manganese(II) sulfate monohydrate, cadmium, sulfanilic acid, and 1-naphthylamine decreased because of the larger sample size.

Tables II and III show typical recoveries obtained by the method for both ppb and ppm levels of nitrate ion. Table II used the series 1 standards. Table III used the series 2 standards.

In the 30 to 420 ppb range an average recovery of 100.4% was obtained with a pooled S.D. of ±5.9%. The graph of these data had a pooled point correlation coefficient, R, of 0.9997. In the 0.5 to 5.0 ppm range an average recovery of 100.0% was obtained with ±1.7% S.D. and a 0.9999 correlation coefficient. These values compare favorably with Lambert and DuBois' analyses in the 1.5 to 9.0 ppm range which yielded 100.1% average recovery and ±1.3% S.D. No comparison in the ppb range to the original paper is made since none was reported.

Nitrite correction in our case proved unnecessary since none was found. To determine nitrite we used the recommended procedure of Lambert and DuBois.[1]

The results obtained from the method using 10- and 5-cm cells proved excellent over a range of 30 to 5000 mcg/l nitrate ion, and detection was possible down to 10 ppb. The method was routinely used for a wide range of nitrate concentrations in fresh-water samples for the Lake Erie Environmental Studies Program. The samples included water from both streams and lakes in Chautauqua County, New York.[4] The method was quite successful for this type of routine analysis in view of its facility of use and precision provided.

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TABLE I

Comparison of reagent concentrations

Reagent	Mixed acid reagent (g/ml)		Color developing reagent		Total determination (g/ml)	
			(g/g)	(g/2g)		
	Lambert & DuBois	This paper	Lambert & Dubois	This paper	Lambert & DuBois	This paper
Citric acid	0.040	0.040	—	—	0.024	0.020
Ammonium chloride	0.167	0.180	0.500	1.500	0.120	0.120
Dibasic sodium phosphate	0.00267	0.00267	—	—	0.00160	0.00134
Sodium chloride	0.100	0.180	—	—	0.060	0.090
Copper (II) sulfate	0.000160	0.000373	—	—	0.000096	0.000186
Acetic acid	$0.020\,\frac{\text{ml}}{\text{ml}}$	$0.020\,\frac{\text{ml}}{\text{ml}}$	—	—	$0.012\,\frac{\text{ml}}{\text{ml}}$	$0.010\,\frac{\text{ml}}{\text{ml}}$
Sodium citrate	—	—	0.366	0.366	0.0134	0.0073
Manganese (II) sulfate monohydrate	—	—	0.101	0.101	0.0040	0.0020
Cadmium	—	—	0.030	0.030	0.0012	0.0006
Sulfanilic acid	—	—	0.020	0.020	0.0008	0.0004
1-Naphthylamine	—	—	0.010	0.010	0.0004	0.0002

TABLE II

Precision of the determination of NO_3^- in the ppm range using the recommended procedure

	% Recovery		
ppm NO_3^-	Run A	Run B	Run C
0.500	100.9	100.9	101.2
1.000	97.7	98.9	103.9
1.500	100.5	101.8	98.6
2.000	99.1	100.0	99.8
3.000	102.2	96.6	98.0
5.000	100.4	99.5	100.0

TABLE III

Precision of the determination of NO_3^- in the ppb range using the recommended procedure

	% Recovery		
ppb NO_3^-	Run A	Run B	Run C
30	116.1	99.7	99.7
60	87.2	99.5	103.7
120	101.6	105.7	103.7
180	100.9	94.0	94.0
300	101.2	98.7	100.4
420	101.3	100.1	99.6