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Nitrite Determination in Environmental Samples with an Ion-selective Electrode

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The possibility of using an Orion nitrogen oxide electrode for nitrite determination in environmental samples has been investigated. In samples with nitrite concentration below 0.2 mg/dm^3 the electrode method is inferior to the classical Griess-Saltzman method. However, at higher nitrite levels (above 0.5 mg/dm^3) the electrode method offers advantages because of its simplicity and short determination times. Nitrite concentration determined ranged from 0.020 mg/dm^3 (in river water) up to several mg/dm^3 (in frankfurters).

INTRODUCTION

The nitrite ion is found in the environment only in traces. It can be found either naturally or by its use as a food preservative and a corrosion inhibitor in industrial process water. As an intermediate state of nitrogen, both in the oxidation of ammonia to nitrate and in the reduction of nitrate, it almost never occurs in pure water. At the most it can occur up to 0.01 mg/dm^3 .¹ In polluted water nitrite levels are around 0.2 to 2.0 mg/dm^3 ,¹ so that the nitrite content, along with that of nitrate, ammonia and phosphate ions, is one of the most important indicators for the extent of water pollution and eutrophication.

The toxicity of nitrite is well known. It oxidizes hemoglobin to methemoglobin which is unable to transport oxygen, and death results from anoxias in severe cases². As a result of current environmental awareness concern has frequently been expressed in connection with the role of the nitrite ion as an important precursor in the formation of *N*-nitrosamines, many of which have been shown to be cancerogenic, mutagenic or teratogenic^{3,4}. The allowable limit for nitrite in potable water in Yugoslavia is $0.05 \text{ mg NO}_2^- \text{—N/dm}^3$ ⁵. Therefore, it is important that sensitive and accurate methods are available for the determination of this ion.

Nitrite is usually determined spectrophotometrically after reaction with various coupling reagents⁶⁻⁹. A summary and comparison of these methods have been reported by Szekely¹⁰, and Sawicki et al.¹¹. The standard method for nitrite determination in water and wastewater¹² involves the formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by the coupling of diazotized sulfanilic acid with *N*-(1-naphtyl)-ethylene diamine dihydrochloride. The method is recommended for the 0.005 to 0.050 mg/dm^3 concentration range.

Recently, an accurate and sensitive determination (down to 0.0003 mg/dm^3) of the nitrite ion by differential pulse polarography has been described¹³.

Although ion-selective potentiometry has become a well established analytical method in the last few years¹⁴⁻¹⁶ little has been published about nitrite determination by ion-selective electrodes. Guilbault¹⁷⁻¹⁸ used an immobilized enzyme electrode for accurate determination in the 10^{-4} to $5 \cdot 10^{-2} \text{ mol/dm}^3$ range, and Tabatabai¹⁹ analyzed nitrite in soil extracts and water samples by using an Orion nitrogen oxide electrode.

The aim of this paper, therefore, is to investigate the analytical efficacy of the nitrogen oxide specific electrode in analysis of some environmental samples, and to compare it with the results of the spectrophotometric measurements.

EXPERIMENTAL

Apparatus

The nitrogen oxide electrode used was an Orion 95-46 gas sensing electrode. With this electrode, having itself an internal reference electrode, no external reference electrode is required. Orion filling solution 95-46-02 was used in the inner reference compartment. Potential measurements were read from an Orion Model 701A Digital pH/mV Meter. All measurements were carried out at room temperature kept constant at $300 \pm 3 \text{ K}$. It is important that the samples, standards and the electrode are at the same temperature. A teflon coated magnetic stirrer was used to stir the solution. To minimize temperature fluctuation caused by heat from the stirring motor a piece of styrofoam was placed beneath the beaker. Absorbance readings in the spectrophotometric method were made on an Unicam Model SP 600 spectrophotometer with 1 cm cells.

Reagents

All chemicals were reagent grade and used as supplied. Distilled and deionized water was used to prepare all solutions. Stock nitrite solution ($1000 \text{ mg NO}_2/\text{dm}^3$) was prepared by weighing 1500 mg sodium nitrite, which had previously been dried at 110°C , and dissolving it into a volumetric flask. It was standardized against standard $0.01 \text{ mol/l}^3 \text{ KMnO}_4$ solution. Standard nitrite solutions were prepared daily by serial dilution of the $1000 \text{ mg NO}_2/\text{dm}^3$ standard. To adjust solution pH and osmotic strength an acid buffer solution was made and used according to the procedure given in the instruction manual supplied with the electrode. Between measurements the electrode was kept in a storage solution made by a 10-fold dilution of the acid buffer solution.

The sulfanilic acid and naphthylamine hydrochloride reagents were prepared for the spectrophotometric measurements, and the determinations of nitrite was performed as usual²⁰.

For the nitrite analysis in water, a series of 1 dm^3 River Bosna water and Sarajevo city sewage grab samples were taken in the middle of the stream and at mid-depth. Samples were analysed the same day, or kept overnight in a refrigerator. Filtration, if necessary, was performed by using nitrite-free Whatman No. 1 filter paper.

Frankfurters and liver paste were prepared for analysis by using the official method for analysing of meat, fat, and oil products²¹.

Procedure

For higher nitrite levels (above 0.5 mg/dm^3) use direct measurements. Make a series of nitrite standards that will bracket the unknown concentration. Use tall beakers that minimize the ratio of surface area to volume. Place a $100 \mu\text{m}^3$ mid-range standard in a $150 \mu\text{m}^3$ beaker. Add stirring bar, and adjust stirrer motor to give rapid mixing without forming a vortex. Place electrode in the standard and add $100 \mu\text{m}^3$

acid buffer. Wait for a stable reading and record. Rinse electrode, blot dry, and place in the most dilute standard. After the electrode has come to equilibrium, record the potential. Repeat the above with the most concentrated standard. Rinse electrode and place in the unknown sample. Wait for a stable reading and record. Prepare the calibration curve and determine the concentration of the unknown.

For low nitrite levels (below 0.5 mg/dm^3) use the known addition method. Add a known standard (about 10 times as concentrated as the sample) to a sample and observe the potential change before and after the addition. From the electrode slope, change in potential and the concentration of added standard, determine the sample concentration.

For low-level measurements use fresh, deionized water. If the sample contains free carbon dioxide remove it prior to measuring by adjusting the sample pH to 5.5 with 2.5 mol/dm^3 perchloric acid.

RESULTS AND DISCUSSION

Electrode exhibits Nernstian response to nitrite concentrations in the 0.5 to 230 mg/dm^3 range, with faster response at higher nitrite levels. Electrode response (in mV, relative to the $1.0 \text{ mg NO}_2^-/\text{dm}^3$ standard) at low nitrite concentrations is shown in Figure 1.

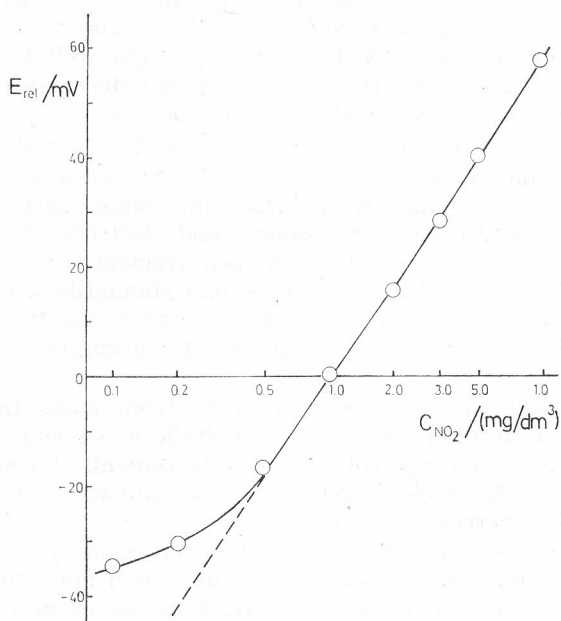


Figure 1. Electrode response at low nitrite concentrations.

When low concentrations are being determined the electrode should be allowed to come to equilibrium before the standard addition is made. Otherwise, the resulting analysis value will be inaccurate, as the analysis results will be too high. Electrode response times for different standard solutions are listed in Table I.

TABLE I
Time Required for Electrode Equilibration

$c\text{NO}_2^-$ /(mg/dm ³)	Equilibration time/minute
0.10	90
0.20	75
0.50	40
1.0	20
2.0	15
3.0	12
5.0	11
10	10
50	6
100	4

It is obvious (Table I) that direct analysis below 0.5 mg NO₂⁻/dm³ requires long equilibration times. At these low levels the probability of sample contamination may increase due to the probability of leaching of a small amount of nitrite from the internal filling solution. The leaching rate, shown as an excessive meter drift, appears to effectively limit the use of the electrode to samples above 0.5 mg NO₂⁻/dm³. Analysis at sub mg/dm³ levels is so time consuming that direct analysis is impractical. The standard addition method should be used for such samples. However, it works well for nitrite levels down to only about 0.2 mg/dm³. If still lower level determinations are desired various nitrite preconcentration methods could be used.

For a given concentration of nitrite in solution, the partial pressure of the dissolved gaseous anhydrides of nitrous acid, and therefore the electrode response, is a function of sample temperature and osmotic strength. As part of the analysis procedure therefore, the sample and electrode should be allowed to come to ambient temperature before the measurement is made. The addition of the recommended acid buffer to samples and standards will automatically adjust them to the correct osmotic strength, equal to that of the internal filling solution (0.5 osmolal). Samples with higher osmotic strengths should be diluted before measuring.

Potential electrode interferences can arise from gases that react with water to form acidic solutions. Among such volatile weak acids carbon dioxide is the most significant in low level nitrite measurements. It should therefore, be removed by using fresh deionized water, and adjusting the sample pH to 5.5 with 2.5 mol/dm³ perchloric acid.

Several common anions occurring in water were studied as possible causes of interferences in the nitrite analysis. To evaluate their net influence electrode measurements were made in a variety of synthetic solutions containing from 1 to 20 mg NO₂⁻/dm³, and varying amounts of nitrate, chloride, bicarbonate and carbonate. As expected, nitrate and chloride showed no interference. Bicarbonate and carbonate (Table II) did not significantly alter the values of the nitrite content even when untreated for CO₂ removal. Thus, it can safely be said that common anions in water do not interfere in the nitrite determination.

To test the accuracy of the electrode method for nitrite analysis in water, a series of 1 dm³ River Bosna and Sarajevo city sewage grab samples were analysed for nitrite content by both the electrode and by the spectrophoto-

TABLE II

Carbonate and Bicarbonate Interference in Nitrite Determination by Ion-Selective Electrode

Anion Added mg/dm ³	Nitrite Added/(mg/dm ³)				
	0	1	5	10	20
	Nitrite Found/(mg/dm ³)				
Carbonate					
5	0.00	1.00	5.00	9.60	19.70
10	0.00	1.00	5.00	9.60	19.70
50	0.00	1.00	5.00	9.80	19.80
Bicarbonate					
50	0.00	1.10	5.00	10.10	20.00
150	0.00	1.20	5.10	10.40	20.00
250	0.00	1.30	5.10	10.20	20.00

metric method²⁰. Nitrite levels were such that in most samples the electrode method could not successfully compete with the spectrophotometric measurement due to its poor sensitivity. Even in sewage samples nitrite concentration seldom reached 0.5 mg/dm³ or more, the concentration levels at which the electrode method is just at its lowest working range. Therefore, the previous earlier claim¹⁹ that the nitrogen oxide electrode was found satisfactory for nitrite determination in water samples is somewhat surprising.

In order to find and analyse samples with higher nitrite levels, frankfurters and liver paste from different manufacturers were examined. The filtrates obtained by the official method for nitrite analysis in processed meat were divided into two portions. One was analysed by the electrode method, and the other by the spectrophotometric method using *N*-1-naphtylamine as reagent (the Griess-Saltman reaction). The results are shown in Table III. Nitrite content, which for a 10 g sample translated into 0.007% and 0.0003% in frankfurters and liver paste, respectively, was well below the stated level (0.01%).

It is obvious that the agreement between the two methods is quite satisfactory. In fact, the electrode method in such cases may be superior to the spectrophotometric method because of the simplicity of the experimental

TABLE III

Analysis Accuracy vs Naphtylamine Method^a

Sample	Method	
	Electrode	Naphtylamine
Sewage Water	0.36	0.29
River Bosna	—	0.020
Liver Paste		
— Sample A	—	0.15
— Sample B	—	0.10
Frankfurter	3.18	2.94

^a All values are mg NO₂/dm³

set up and the relatively simple chemistry, which is in this case only comprised of the adjustment of the ionic strength of the sample.

Apart from the samples used in this work, the potential electrode can be used in other environmental samples such as the determination of nitrogen dioxide in integrated air samples and measurement of nitrate after conversion to nitrite. The latter seems particularly attractive in view of no chloride interferences as is usually the case in the determination of nitrate by the ion-selective electrode²². Results of preliminary research are encouraging and will be subsequently reported.

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REFERENCES

1. K. Höll, *Water*, de Gruyter, Berlin, 1972, p. 69.
2. O. Bodansky, *Pharmacol. Rev.* **3** (1951) 144.
3. I. A. Wolff and A. E. Wasserman, *Science* **177** (1972) 15.
4. *Chem. Eng. News*, July 31 (1978), p. 20.
5. *Sl. list SFRJ*, **8** (1978) 185.
6. J. A. Dougherty and G. A. Laban, *Anal. Chem.* **47** (1975) 1130.
7. B. S. Garg, Y. L. Mehta, and M. Katyaj, *Talanta* **23** (1976) 71.
8. F. Celardin, M. Marcantonatos, and D. Monnier, *Anal. Chim. Acta* **68** (1974) 61.
9. K. Toe and T. Kiyose, *Anal. Chim. Acta* **88** (1977) 125.
10. E. Szekely, *Talanta* **15** (1968) 795.
11. E. Sawicki, T. W. Stanley, I. Phaff, and A. Domico, *Talanta* **10** (1963) 641.
12. *Standard Methods for the Examination of Water and Wastewater*, APHA, New York, 1975, p. 434.
13. S. K. Chang, R. Kozeniauskas, and G. W. Harrington, *Anal. Chem.* **49** (1977) 2272.
14. R. P. Buck, *Anal. Chem.* **48** (1976) 23R, 50 (1978).
15. J. Koryta, *Anal. Chim. Acta* **61** (1972) 329, 91 (1977) 1.
16. P. L. Bailey, *Anal. Chem.* **50** (1978) 698A.
17. G. G. Guilbault, *Anal. Chim. Acta* **80** (1975) 209.
18. Chih-Hen Kiang, S. S. Kuan, and G. G. Guilbault, *Anal. Chem.* **50** (1978) 1319.
19. M. A. Tabatabai, *Commun. Soil. Sci. Plant Anal.* **5** (1974) 569.
20. *Deutsche Einheitsverfahren zur Wasser Untersuchung*, 7 Lieferung, Verlag Chemie, GmbH, Weinheim/Bergstr. 1975, s. D 10.
21. *Sl. list SFRJ*, **25** (1973) 834.
22. H. Shechter and N. Gruener, *J. Amer. Water Works Ass.* **68** (1976) 543.

SAŽETAK

Određivanje nitrita u uzorcima iz čovjekove okoline

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Ispitana je mogućnost korištenja Orionove nitrogen-oksidgelektrode za analizu nitrita ispod 0,2 mg/dm³, potenciometrijska metoda inferiorna je u odnosu na klasičnu Griess-Saltzman-ovu metodu. Međutim, pri većim koncentracijama nitrita (iznad 0,5 mg/dm³) potenciometrijska metoda pogodnija je zbog jednostavnosti i brzine određivanja. Nađene koncentracije nitrita kretale su se od 0,020 mg/dm³ (u riječnoj vodi) do nekoliko mg/dm³ u hrenovkama.

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