Short Communication

Potentiometric method for the determination of nitrate in ill-characterised water

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Abstract

Ion-selective electrode produces nitrate determination results in good accord with the standard uv method if one follows recommended procedure and meticulously controlled laboratory conditions. The technique is laborious if different types of ill-characterised water samples are examined in the same series but it is practical and rapid when many samples belonging to same source are to be compared or when continuous monitoring of a water supply with known mineralization is required.

1. Introduction

Nitrate content of waters is receiving considerable attention because of potential human and health hazards. A great variety of methods are available for nitrate determination in waters such as reduction to ammonia or nitrite followed by titration[1] or colorimetry[2], ultraviolet spectrophotometry[3] and polarographic technique[4] but all these are time-consuming and suffer from serious interferences, hence are listed as tentative in standard methods for the examination of water[5]. During the past few years, an ion-selective electrode has been developed which is intended to provide a direct measure of the concentration of nitrate ion in aqueous systems[6]. However, direct potentiometric determination of nitrate in ill-characterised waters may be difficult because it is necessary to take into account both ionic strength for activity coefficient correction and interfering

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anions for increased potential elimination. Hence, a study was undertaken to establish the analytical efficacy of nitrate ion-selective electrode in analysis of some waters characterised by high mineralization. The electrode measurements are compared with results of ultra-violet spectrophotometric method.

2. Experimental

2.1. Instruments

Potential measurements were read from a microprocessor based mv meter (Orion, model 901). A liquid membrane type nitrate ion-selective electrode (Orion, model 93-07) was used along with a double junction reference electrode (Orion, model 90-02) bridged with saturated sodium sulfate solution. A magnetic stirrer having a speed control knob was used for stirring of solutions.

2.2. Reagents

A stock solution containing 100 mg/litre nitrate as nitrogen was prepared from analytical reagent grade sodium nitrate (previously dried at 120° C). Standard nitrate solutions were prepared by diluting appropriate amounts of stock solution. To keep a constant ionic strength of samples and standards, an appropriate amount of stock sodium sulfate solution containing 5,000 mg/l as sulfate was added. Interference studies were carried out using sodium salts of bicarbonate, carbonate, chloride, dihydrogen phosphate, nitrite, sulfide and sulfate as sources of interfering anions.

2.3. Sample analysis

The procedure for nitrate measurement with the electrode was as follows :

The concentration of chloride was determined and was removed from solution by quantitative precipitation with silver sulfate (0·02 M). The ionic strength of sample solution was estimated from specific conductance measurements. Before reading the potential of sample solution or of a group of samples with about the same ionic strength, potentials of three standard nitrate solutions differing in concentration by a factor of 10 (1 mg/l, 10 mg/l and 100 mg/l nitrate nitrogen) and having same total ionic strength were measured. The relationship between nitrate concentration of standardising solution and potential was plotted on semilog paper, finally the electrodes were placed in sample solution and the potential observed was converted to nitrate concentration by using the calibration curve. Between measurements, electrodes after rinsing were blotted dry with absorbent tissue.

3. Results and discussion

3.1. Electrode equilibration and stirring effects

Stirring of solution reduces the time taken to reach equilibrium. High stirring rate introduces air bubbles into solution, causing unstable electrode potential, because air

bubbles accumulate on the surfaces of electrode and decrease contact with solution. Therefore, continuous and reproducible stirring was necessary. Under the standardised conditions stirring uniformly with a small PTFE stirring bar equilibrium reached after one minute. The depth of immersion of electrodes in solution was kept constant while changing from standard to sample solution.

3.2. Temperature effects

The slope factor in Nernst equation relating the nitrate concentration and electrode potential is temperature dependent. Hence, measurement of samples and standards was carri·d out at the same temperature. As magnetic stirrer motors impart heat after prolonged use, the beaker containing solution was insulated by keeping a layer of polystyrene foam between the beaker and stirrer.

3.3. Ionic strength

To test if nitrate ion activity measurements are influenced by ionic strength of the solution, a series of measurements were carried out for solutions containing 10 mg/l nitrate as nitrogen and varying sodium sulfate concentrations. Sodium sulfate was chosen as the ionic strength adjustor because it has properties of high ionic strength, good equitransference and sulfate anion has insignificant interference for nitrate electrode. The calibration of electrode was made by standard solution of nitrate containing 500 mg/l of sodium sulfate. The measured nitrate content was found smaller with increasing sodium sulfate concentration.

To avoid influence of ionic strength for nitrate ion activity measurements, the ionic strength of samples was estimated by measuring electrical conductance and then the concentration of nitrate in sample can be determined by calibrating electrode with a standard solution, prepared in sodium sulfate solution having an identical conductivity value as of sample.

3.4. Anion interference

To evaluate the influence of most common anions occurring in water, electrode measurements were made in a variety of synthetic solution containing from 1 to 25 mg/l nitrate nitrogen and varying amounts of hydrogen carbonate, carbonate, chloride' dihydrogen phosphate, nitrite, sulfide and sulfate. The results showed that the interference from phosphate, carbonate and bicarbonate are minor. Sulfate does not interfere at all even at very high concentrations. But there are major additive influences from nitrite, sulfide and chloride. However, nitrite is seldom present in high concentrations in waters, sulfide also seldom reaches as high as 50 mg/l. As to the strongly interfering chloride, it must be initially removed by precipitation with silver sulfate for accurate determineations.

Removal of interference is a problem because excess of removing agent may increase sample ionic strength. To avoid this concentration of interfering chlorides must be

known prior to their removal by precipitation. The advantage is that after this precipitation sodium sulfate is formed in the sample solution and same ionic strength adjustor is added in standard solutions prepared for calibration.

3.5. Comparison with ultraviolet method

Parallel determination of nitrates was performed on well water samples by both the ultraviolet (uv) absorption method (at 220 nm) and the described ion selective electrode (E) method. The ranges of nitrate as nitrogen were found varying between 1·5 and 50 mg/l, most of the samples having between 5 and 30 mg/l. The mineralization of samples varied largely but was mostly high. The chlorides varied between 50 and 500 mg/l ; most of the samples contained around 200 mg/l chlorides. The results of this comparison are summarised in Table I.

The results of nitrate determination by electrode method were compared with those of uv method, as a function of conductivity and of nitrate level. The percentage differences between the two methods are presented in Table II. The differences are more in the samples with low nitrate content (< 5 mg/l) and high salt content (conductivity > 1·0 m mho). The differences are lower in samples with high nitrate concentration; however, the mean differences do not exceed 10 per cent.

Table I

Comparison of electrode (E) method and ultraviolet (UV) method for nitrate determination in samples

Nitrate/nitrogen level range, mg/l	Nitrate found mg/l		Conductivity m mho/cm		Chlorides mg/l	
	E	UV	Min.	Max.	Min.	Max.
< 5·0	3·9	3·3	0·6	1·3	41	110
5·0–10·0	7·8	7·1	0·7	2·1	79	260
10·0–20·0	16·2	14·7	0·8	2·5	134	330
20·0–30·0	29·3	27·0	0·9	2·7	195	490
> 30·0	38·9	37·8	1·2	3·3	400	560

Table II

Mean difference between the results obtained by UV and electrode methods correlated with levels of nitrate and conductivity values

Nitrate/ nitrogen level range mg/l	Mean difference, %		
	Conductivity level range m mhos/cm		
	0·61–2	1·2–2·0	2·0–3·0
1–10	5·6	9·2	19·6
10–20	4·3	6·6	12·8
20–30	3·0	5·3	7·4
30–40	2·4	3·8	4·4

4. Conclusions

The results obtained by electrode method in highly mineralized waters under laboratory conditions, including removal of chlorides, are in agreement with those obtained by uv method. However, they are somewhat higher than those of uv method especially in the range of low nitrate concentrations and high salt contents. The electrode method for accurate nitrate determination is not a field method, because complex controls are required to obtain reliable results. In water of low mineralization, electrode method can be used as a screening method to identify the content of nitrate. In water of high mineralization, it needs standardisation with solution of same order of ionic strengths as the samples. Therefore, electrode method is laborious when different types of water samples are to be examined in the same series but it is practical and rapid when many samples belonging to a same source are to be compared or when continuous monitoring of a water supply with known mineralization is required.

Acknowledgement

References

1. BREMNER, J. M. AND   J. Agric. Sci., 1955, 46, 320.
   SHAW, K.

2. Litchfield, M. H.   *Analyst*, 1967, **92**, 132.

3. Navone, R.   *J. AWWA*, 1964, 56, 781.

4. Frazier, R. E.   *J. AWWA*, 1963, 55, 624.

5.   APHA, AWWA, WPCF, *Standard methods for the examination of water and waste water*, 14th edn., Washington, 1975.

6. Potterton, S. S. and Shults, W. D.   *Anal. Lett.*, 1967, 1, 11.