The automated determination of nitrate in water

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Abstract

An automated method for the determination of nitrate at low concentrations in water was developed. Nitrate was reduced to nitrite using an on-line cadmium reductor followed by the colorimetric determination of the nitrite according to the Shinn method. The reductor consisted of a copperised cadmium column with a small inner diameter which limits sample dispersion. Two variations of the method were evaluated, both showing good accuracy and precision. At a sampling frequency of 100/h the carry-over was better than 1%.

Introduction

The direct determination of nitrate in water is difficult for the following reasons:

- relatively complex procedures required;
- high probability that interfering constituents will be present; and
- the limited concentration ranges of the various techniques (Standard Methods, 1985).

Due to these limitations a number of indirect methods have been developed. The most common indirect method is based on the reduction of nitrate to nitrite with subsequent colorimetric determination of the nitrite formed (Mullin and Riley, 1955). This method has been automated and adapted for a flow injection analytical (FIA) system (Anderson, 1979). A variety of reducing agents have been proposed for the automated reduction including titanium (III) chloride (Al-Wehaid and Townshend, 1986), mercury (II) (Anwar *et al.*, 1986), hydrazine sulphate (Kamphake *et al.*, 1967) and cadmium (Van Staden *et al.*, 1986).

Cadmium and hydrazine sulphate are often used for nitrate reduction. A number of constituents in natural water, however, interfere during the hydrazine sulphate reduction (Downes, 1978). The automated cadmium reduction is performed either with a column (Anderson, 1979) or tube (Van Staden *et al.*, 1986) reductor. The catalytic effect of copper is known and utilised in most methods today (Lambert and Du Bois, 1971). A disadvantage of the cadmium reduction methods is the large dispersion of the sample in the reductor, lowering the sampling frequency (Anderson, 1979; Van Staden *et al.*, 1986).

This article describes an indirect flow-injection method for the determination of low level nitrate in water. The cadmium reduction method is used with a copperised cadmium column. Sample dispersion is limited by the small inner diameter (i.d.) of the reductor tubes, thus maintaining a high sampling frequency.

Experimental

The analytical flow system is shown in Fig. 1.

Apparatus

A Technicon AutoAnalyzer Sampler IV with a modified sampling switching mechanism was used to present samples to an Auto Analyzer Model II peristaltic pump fitted with standard Technicon pump tubes. A Technicon AutoAnalyzer double channel colorimeter with a 50 mm debubble type flow cell (i.d. = 1,5 mm) was connected to a standard Technicon recorder. A liquid chromatography valve (Carle model 2014) with two variable sample loops was used to inject samples into the carrier stream. The valve was driven by a valve motor unit (Carle model 4201) con-

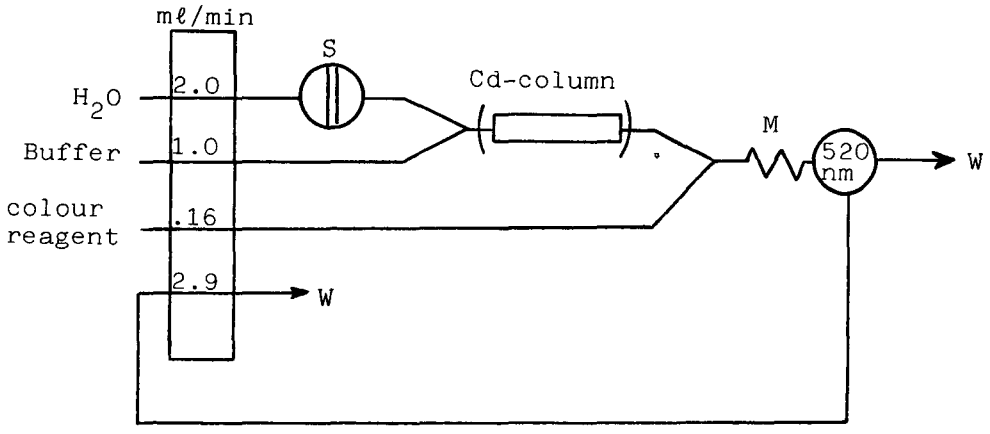

Figure 1
Schematic diagram of the analytical flow system. S = sampling valve; M = mixing coil; D = debubbler; W = waste.

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trolled by a locally constructed timing device which switched both the valve and sampler at appropriate intervals.

Cadmium reductor

The cadmium reductor consists of a 300 mm copper tube (i.d. = 0,35 mm) followed by a 100 mm cadmium column. The column is prepared as follows: The nose piece of a pasteur pipet (i.d. = 1,2 mm and length of 100 mm) is filled with cadmium granules (diameters between 0,3 and 0,5 mm) and the ends plugged with glass wool.

Reagents

AR grade reagents and deionised water was used. Colour reagent A: Dissolve 40 g sulphanilamide ($NH_2C_6H_4.SO_2NH_2$) and 2 g N-(1-Naphtyl)-ethylene diamine dihydrochloride ($C_{12}H_{16}Cl_2N_2$) in 500 mℓ water. Add 100 mℓ phosphoric acid and dilute to 1 ℓ with water. Colour reagent B: (1:7 dilution of colour reagent A) Dilute 125 mℓ of colour reagent A to 1 ℓ with water. Copper solution: Dissolve 19 g EDTA (disodium salt) and 6,3 g copper sulphate in 350 mℓ water. Set the pH to 7,0 with 2,0 mol/ℓ sodium hydroxide solution and dilute to 500 mℓ with water. Nitrate standard solutions: Dry potassium nitrate (KNO_3) for 1 h at 105°C. Weigh 0,7255 g KNO_3 and dissolve in water. Prepare the following standard solutions from the stock nitrate solution: 0,1; 0,4; 0,5; 1,0; 2,0; and 4,0 mg/ℓ NO_3^- - N.

Method optimisation

No sensitivity optimisation was performed since the sensitivity for the required range was acceptable using the 50 mm flow cell. The calibration curve, however, deviated significantly from linearity under these conditions (Fig. 2). It was thought initially that this deviation from linearity at the higher nitrate concentrations was due to the inability of the reduction column to reduce the nitrate completely. Nitrite standard solutions in the same concentration range were prepared and analysed. This calibration curve experienced the same deviation at the higher nitrite concentrations. The influence of colour reagent dilutions on the linearity of the calibration curve was subsequently examined. A number of colour reagent dilutions were prepared and calibration curves were drawn up for each dilution. There was a definite improvement in the linearity of the calibration curve at the higher colour reagent dilutions, although the sensitivity decreased substantially (Fig. 2). A compromise between linearity and sensitivity was chosen at a 1:7 colour reagent dilution (see **Reagents**).

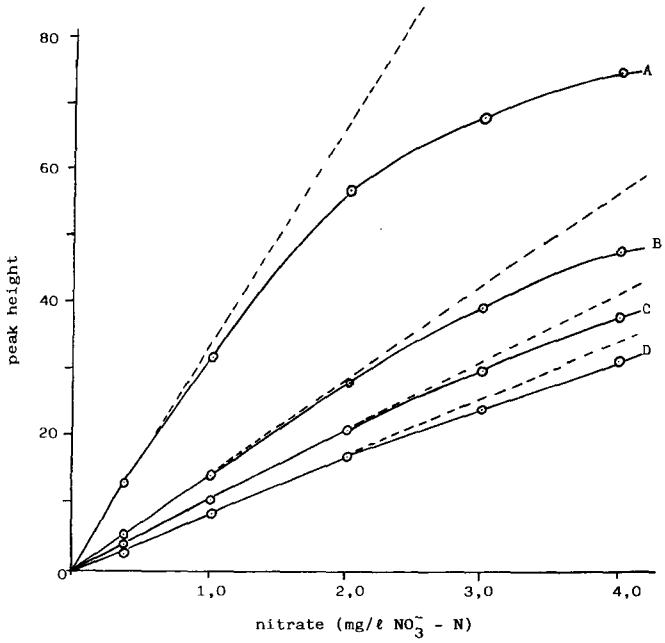

Figure 2
The influence of colour reagent dilutions on the linearity and sensitivity of the cadmium reduction method. A = no dilution; B = 1:6 dilution; C = 1:7 dilution and D = 1:8 dilution of the colour reagent.

Method evaluation

The cadmium reduction method was evaluated at two colour reagent concentrations:

- a variation using the initial colour reagent; and
- a 1:7 dilution of the original colour reagent.

The precision of the method was examined in the range 0,4 to 4,0 mg/ℓ (NO_3^- - N). The results are shown in Table 1. The precision of both variations was better than 1% over this range. Fig. 3 is a recording chart of a number of repetitions of the highest nitrate concentration (with the initial colour reagent).

A number of surface and ground-water samples were analysed using this FIA method and a segmented flow analytical (SFA) method (Van Vliet *et al.*, 1986). The results of the two variations of the FIA method compare favourably with those of the segmented flow method (Table 2). Recovery tests on a number of surface and ground-water samples were performed. The average recoveries of the two FIA variations were 99,0 and 99,5% respectively (Table 3).

Nitrite obviously interferes with the indirect nitrate determination. Nitrite, however, generally occurs in most surface and ground waters only at low concentrations (Bouwer, 1978). Certain polluted waters can have a high nitrite concentration, however, in which case the concentration must be reported as the sum of nitrate and nitrite. The colour forming reactions with nitrite are specific and no interferences are expected. High recoveries have been reported (Hendriksen and Selmen-Olsen, 1970). The influence of a number of metals on the reduction process was examined. Standard nitrate solutions (containing 2 mg/ℓ NO_3^- - N) were prepared containing respectively 10 mg/ℓ Fe(II), Fe(III) and Mn(II). The solutions were examined with a difference between the calculated nitrate concentrations of less than 1%. Since mercury(II) chloride is often used for the preservation of samples, its influence on the reduction process was examined. Two sets of standard solutions were prepared, the one containing only nitrate while the other had a mercury(II) chloride concentration of 20 mg/ℓ. Both sets were examined with the two variations of the method and almost identical results were obtained.

The carry-over between consecutive samples was examined at different sampling frequencies. The concentration of a sample (with a low nitrate concentration) was determined. The same sample was then reanalysed consecutively after three samples of higher nitrate concentrations. The carry-over was calculated as the percentage difference between the two values for the sample. The results from a number of combinations are shown in Table 4. At a sample frequency of 100/h the carry-over between the highest nitrate concentration (4,0 mg/ℓ) and a solution containing 0,4 mg/ℓ

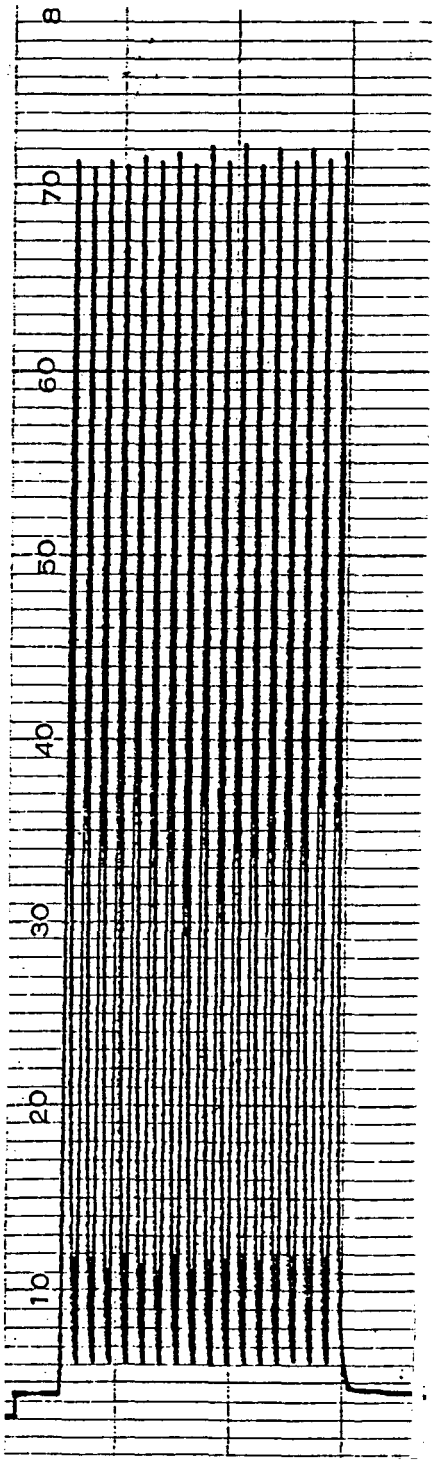

Figure 3
Recorder chart of a number of repetitions of the highest nitrate standard solution.

TABLE 1
THE PRECISION OF THE TWO VARIATIONS OF THE METHOD IN TERMS OF STANDARD DEVIATION USING: THE VARIATION WITH THE INITIAL COLOUR REAGENT (a); AND THE 1:7 DILUTION OF THE COLOUR REAGENT (b)

	Nitrate concentration (mg/ℓ NO_3 - N)	Standard deviation (%)
(a)	4,0	0,20
	2,0	0,32
	1,0	0,46
	0,4	0,80
(b)	4,0	0,81
	2,0	0,92
	1,0	0,71
	0,4	0,61

TABLE 2
COMPARISON BETWEEN THE RESULTS OBTAINED FROM THE ANALYSIS OF SURFACE AND GROUND-WATER SAMPLES USING THE TWO FIA VARIATIONS: INITIAL COLOUR REAGENT (a); A 1:7 COLOUR REAGENT DILUTION (b) AND A SEGMENTED FLOW ANALYTICAL (SFA) METHOD

Nitrate concentration (mg/ℓ NO_3 - N)		
(a)	(b)	(SFA)
0,32	0,33	0,33
0,11	0,11	0,14
0,03	0,02	0,03
0,40	0,43	0,43
0,12	0,12	0,15
0,93	0,90	0,94
0,40	0,40	0,42
3,13	3,12	3,20

TABLE 3
THE RECOVERY OF NITRATE IN A NUMBER OF SURFACE AND GROUND-WATER SAMPLES USING A SPIKING METHOD FOR THE VARIATION WITH INITIAL COLOUR REAGENT (a); AND A 1:7 DILUTION OF THE COLOUR REAGENT (b)

	Expected (mg/ℓ)	Obtained (mg/ℓ)	(%)	Recovery
(a)	1,18	1,16		98,3
	1,05	1,02		97,1
	1,23	1,20		97,6
	1,07	1,06		99,1
	1,43	1,47		102,7
			average	99,0
(b)	1,20	1,17		97,5
	1,03	1,02		99,5
	1,23	1,22		99,2
	1,07	1,08		100,1
	1,45	1,47		101,4
			average	99,5

TABLE 4
CARRY-OVER BETWEEN CONSECUTIVE SAMPLES WITH RESPECTIVELY A HIGH AND A LOW NITRATE CONCENTRATION

Frequency (samples/h)	Nitrate conc. ($mg.\ell^{-1}$ NO_3-N)		Carry-over (%)
	high	low	
100	4,0	1,0	1
	1,0	0,4	1
120	4,0	1,0	1
	4,0	0,4	4
150	4,0	1,0	4
	4,0	0,4	15

was less than 1%. The carry-over, however, is substantially higher at a frequency of 150 samples/h (Table 4). This frequency can be useful where samples contain more or less the same nitrate value or where there can be compromise for the carry-over.

Discussion

Both variations of the cadmium reduction method have a good accuracy, precision and linearity. The sensitivity and precision of the variation with initial colour reagent concentration is better than the variation with the colour reagent dilution, while the latter gave a better linearity. A frequency of 100 samples/h is maintained using this method. This is significantly higher than sampling frequencies that have been reported previously (Anderson, 1979; Van Staden *et al.*, 1986). This advantage makes it suitable for the routine analysis of large numbers of water samples.

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