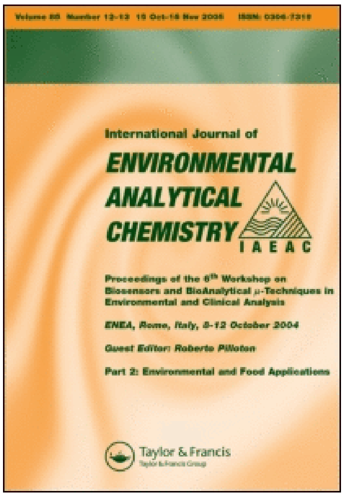

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Determination of Nitrate in Water Containing Dissolved Organic Carbon by Ultraviolet Spectroscopy

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DETERMINATION OF NITRATE IN WATER CONTAINING DISSOLVED ORGANIC CARBON BY ULTRAVIOLET SPECTROSCOPY

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Direct measurement of ultraviolet (UV) light absorption by nitrate in the 200–205 nm wavelength band offers a reliable, accurate and rapid method of nitrate determination in natural waters. However, UV light is also strongly absorbed by organic matter at these wavelengths. A two-wavelength approach was adopted and evaluated for the correction of absorbance that organic matter might have contributed. The measurements were made at 205 nm and 300 nm. The relationship between absorbance at 205 nm and 300 nm due to organic matter was incorporated into traditional nitrate calibration curve to make allowance for the organic matter contribution.

The method developed has a detection limit of 0.04 mg NO_3-N dm^{-3} and is capable of determining nitrate concentration in the range of 0.08 – 4.0 mg NO_3-N dm^{-3}. In terms of accuracy and reproducibility, the method compares well with the hydrazine-reduction method, with matching precision (1.14% over the concentration range) and accuracy (± 2%). This two-wavelength approach based method is rapid, low-cost and does not require any reagents or treatment, and is suitable for waters with dissolved organic carbon (DOC) concentration of up to 20-mg dm^{-3}.

Keywords: Nitrate; Dissolved organic carbon; Salinity; pH; UV absorption

INTRODUCTION

Nitrate (NO_3^-) is considered as one of the important substances to be determined in waters, because of its potential environmental and human health implications[1]. Nitrate in water can be determined by many methods (e.g. nitrate ion selective electrodes, UV spectroscopy, steam distillation following reduction to NH_3, ion chromatography, colorimetric following reduction by Cd, Cd-Cu or hydrazine). While some of the procedures are cumbersome (e.g. steam distilla-

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tion after reduction to NH_3) others involve a substantial investment (e.g. ion chromatography) or pose health and environmental hazards (e.g. those using hydrazine or heavy metals as reductants).

Nitrate ion selective electrodes are simple and cost-effective, and have been widely used and favourably compared with other reference methods[2–5]. However, the selective electrodes are not reliable at low nitrate concentrations, suffer from other anions (e.g. chloride, bromide, nitrite and sulphate) interference and require buffering of samples to a common ionic strength before a reliable nitrate determination can be made[6].

Direct measurement of ultraviolet (UV) light absorption by nitrate ion is recognised as a rapid, easy and accurate method of nitrate determination[7,8]. The UV spectroscopic methods make use of the strong absorption spectrum of nitrate between 200–210 nm. However, ultraviolet light is also strongly absorbed by dissolved organic matter in this wavelength band, and some saline constituents may as well cause interference. Rennie et al.[7] used activated carbon filter to eliminate the interference from organic matter. The method published by the American Public Health Association[8] suggests a two-wave length approach for water containing dissolved organic matter. In this method, the absorbance is measured at 220 nm and, a second measurement at 275 nm where nitrate does not absorb the UV light, is made as a correction for organic matter from that at the shorter wave length. This empirical correction factor is related to the nature and concentration of organic matter and may vary from one type of water to another. The main aim of the study reported in this paper was to further examine the two-wave length approach based UV spectroscopic method with a view to assess its suitability as a low-cost routine laboratory method. An additional aim was to determine nitrate concentrations in a large number of upland waters, and to compare them with those determined by the hydrazine-reduction method.

EXPERIMENTAL

Nitrate and dissolved organic carbon (DOC) stock solutions (100 mg NO_3-N dm^{-3} and 100 mg DOC dm^{-3}) were prepared by dissolving appropriate amounts of AnalaR grade KNO_3 and an in-house synthesised polymaleic acid[9] in de-mineralised water. The stock solutions were kept refrigerated (4°C), and the standard solutions of nitrate and DOC were freshly prepared before their use. Unless otherwise stated no attempts were made to alter the pH and ionic strength of the standard solutions. To assess the effect of pH on the UV absorption spectra, the pH of the standard nitrate solutions was adjusted using either $0.1M$ HCl or 0.1*M* NaOH. Similarly, the effect of saline constituents was evaluated by raising the electrical conductivity to 1000 μS cm^{-1}. NaCl and KCl salts in 1:1 ratio were used for this purpose. Most freshwaters should have their DOC, pH, and electrical conductivity within the ranges used in this study[10].

DOC, pH and conductivity were determined using standard methods for the analysis of water[8]. Nitrate-N was analysed in a large number of freshwater samples by a nitrate-reduction based reference method and by the two-wave length approach based UV spectroscopy method. All freshwater samples were filtered through 0.450-μm membranes prior to their analysis for DOC, pH, electrical conductivity and nitrate-N.

Procedure

Ultraviolet spectra for nitrate-N and DOC were obtained by scanning their standard solutions over a number of wavelengths between 190 and 350 nm. The spectrophotometer (Philips PU 8720 UV-Visible with deuterium light source) was zeroed against de-mineralised water and the maximum absorbance was set at 3.0. The samples were transferred into a 10-mm quartz cuvette and the absorbance was read at a number of pre-set wavelengths. Based on initial scanning, a two-wavelength approach was adopted; a shorter wavelength in the region of 200 nm where both nitrate and organic matter (polymaleic acid) show maximum absorption, and a higher wavelength where the light is absorbed only by organic matter. The absorption by organic matter at the two wavelengths was used to develop an empirical relationship. This relationship was then used to make a correction for the absorbance at the shorter wavelength that dissolved organic matter might have contributed. This two-wavelength approach was first tested on synthetic water samples for nitrate recovery before being applied to a large number of natural waters.

RESULTS AND DISCUSSION

UV-spectra: nitrate, organic matter, salinity and pH effects

Figure 1 shows the absorption spectra of nitrate and organic matter (polymaleic acid) in water. Both nitrate and organic matter exhibited absorption maxima at 200 nm. While organic matter shows a gradual decrease in absorption with increasing wavelength in the range of 200–300 nm (Figure 1b), ultraviolet light absorption by nitrate decreases sharply beyond 210 nm and no absorption

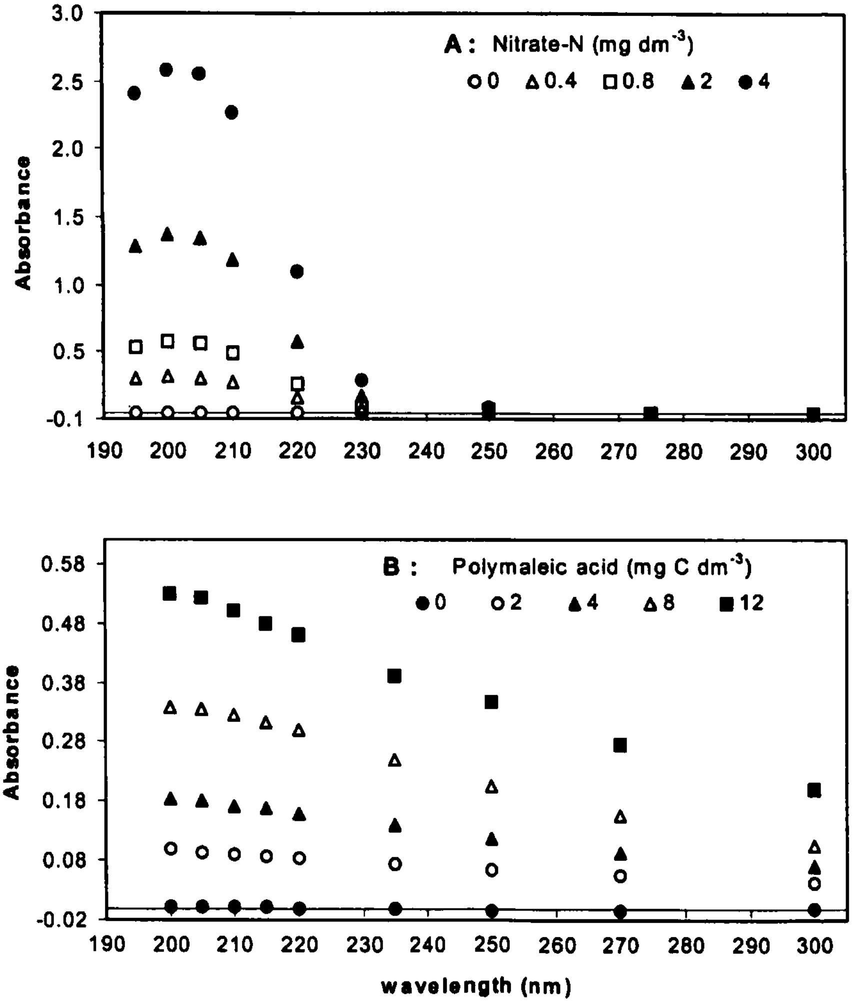

FIGURE 1 Absorption spectra of (a) nitrate (0–4 mg N dm^{-3}) and (b) polymaleic acid (0–12 mg C dm^{-3})

occurred at 300 nm (Figure 1a). For nitrate, the spectra suggest that the light absorption should be measured at 200 nm for maximum sensitivity.

High salt concentration, especially chloride (Cl^-) has been reported to cause interference in the determination of nitrate by various analytical methods, including ion chromatography, nitrate selective electrodes and UV spectroscopy[6]. To test the effect of soluble salts on UV absorption by nitrate, nitrate standard solutions (0.0 – 4 mg NO_3- N dm^{-3}) were spiked with KCl and NaCl to raise their conductivity to 1000 μS cm^{-1}. The spectra were influenced by the raised conductivity (Figure 2a); at 200 nm all solutions, including nitrate-blank, absorbed more light compared to non-saline solutions. However, there was no effect at 205 nm. This is consistent with Dong et al.[11] who found no effect of many commonly occurring salinity constituents on nitrate-UV absorption spectra in the 206–214 nm wavelength band. As most catchment waters will have conductivity lower than 1000 μS cm^{-1}[10], it is reasonable to conclude that saline constituents do not interfere with nitrate-UV absorption spectra provided the measurements are made at 205 nm or some higher wavelength. A wavelength of 205 nm was therefore considered appropriate, as the loss in sensitivity at this wavelength was negligible (Figure 1a). The effect of pH on the absorbance by nitrate was investigated by scanning nitrate standard solutions adjusted to pH 3.1 and 8.5, with 6.1 as the pH of control solutions. The results showed that this change in pH had no effect on the nitrate UV-absorption spectra. Dong et al.[11] also reported no effect of pH on nitrate and nitrite UV-absorption spectra in the pH range of 3.0 – 9.0, a range that will include most natural waters.

The two-wavelength approach

The nitrate and organic matter UV-absorption spectra (Figure 1) and subsequent investigations of the effects of salinity and pH (Figure 2) clearly showed that the first measurement be made at 205 nm. In the method published by the American Public Health Association[8], the first measurement is made at 220 nm. The measurement at 220 nm is recommended, possibly to abate the absorption by other substances. Since there was no interference due either to salinity or to pH, a measurement at 220 nm would unnecessarily have caused a major loss of sensitivity for nitrate determination (Figure 1a). It would therefore appear that in most natural waters the absorbance at 205 nm will be due to nitrate and dissolved organic matter if present. However, a relationship between the absorption due to organic matter at 205 nm and a higher wavelength where nitrate does not absorb the ultraviolet light can be used for making a correction for the absorption at 205 nm that organic matter might have contributed. The measurements at 205 nm and 300 nm showed that the absorbance increased linearly at both wavelengths with increasing concentration of polymaleic acid (Figure 3a), a compound similar to soil organic matter[9]. These relationships remained linear up the maximum concentration (20-mg C dm^{-3}) of the polymaleic acid used. Based upon these measurements, a relationship between the absorbance at 205 nm and 300 nm was developed (Figure 3b):

$$y \text{ (absorbance at 205 nm)} = 2.8414x \text{ (absorbance at 300 nm)} - 0.0126 \quad (1)$$

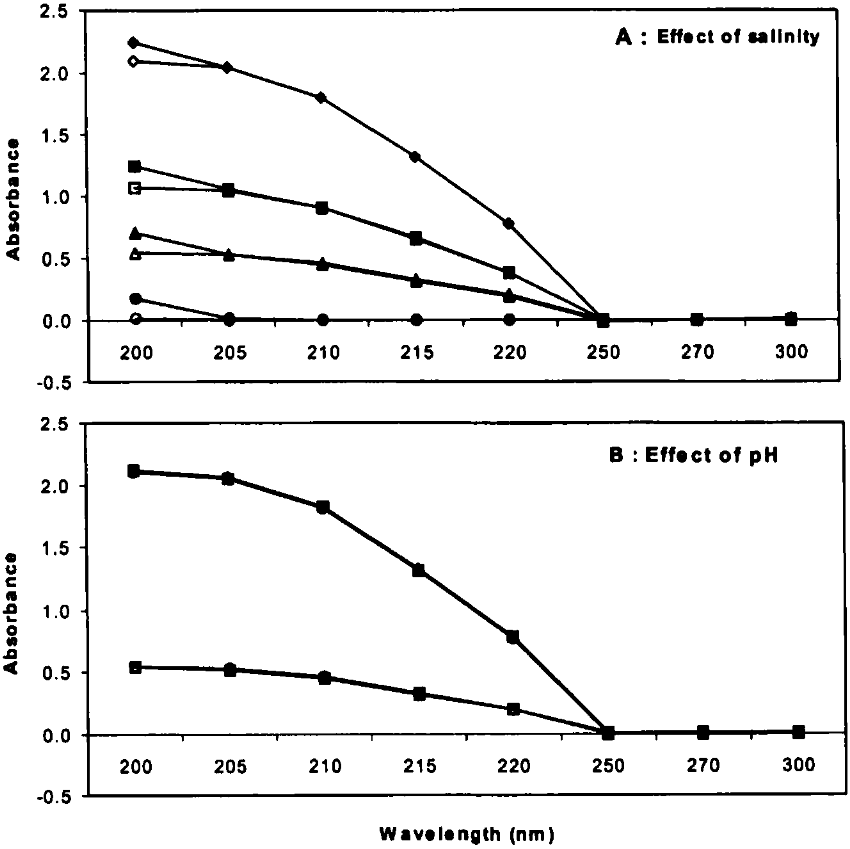

FIGURE 2 Absorption spectra of nitrate-N showing the effects of solution: (a) salinity (filled symbols are for nitrate solutions made in saline water of 1000 μS cm^{-1} and the open symbols are for those made in de-mineralized water; •, ▲, ■ and ♦ relate to 0, 1, 2 and 4 mg NO_3-N dm^{-3}) and (b) pH (open and filled symbols are for 1 and 4 mg NO_3-N dm^{-3} respectively; and •, ■ and ▲ for pH 6.1 as control, and 3.1 and 8.5 respectively)

It is interesting to note that a relationship developed using several nitrate-free naturally coloured waters (Figure 3c) was similar to that developed using the polymaleic acid. It would therefore appear that the polymaleic acid-based relationship is not only logical but may also mimic UV absorption by different types of naturally occurring organic substances in waters.

To test the validity of the two-wavelength approach, recovery percentages were measured by spiking nitrate standard solutions with various organic matter (polymaleic acid) concentrations. The absorbance was read at 205 nm and 300 nm, and the absorbance contributed by the organic matter at 205 nm was deduced

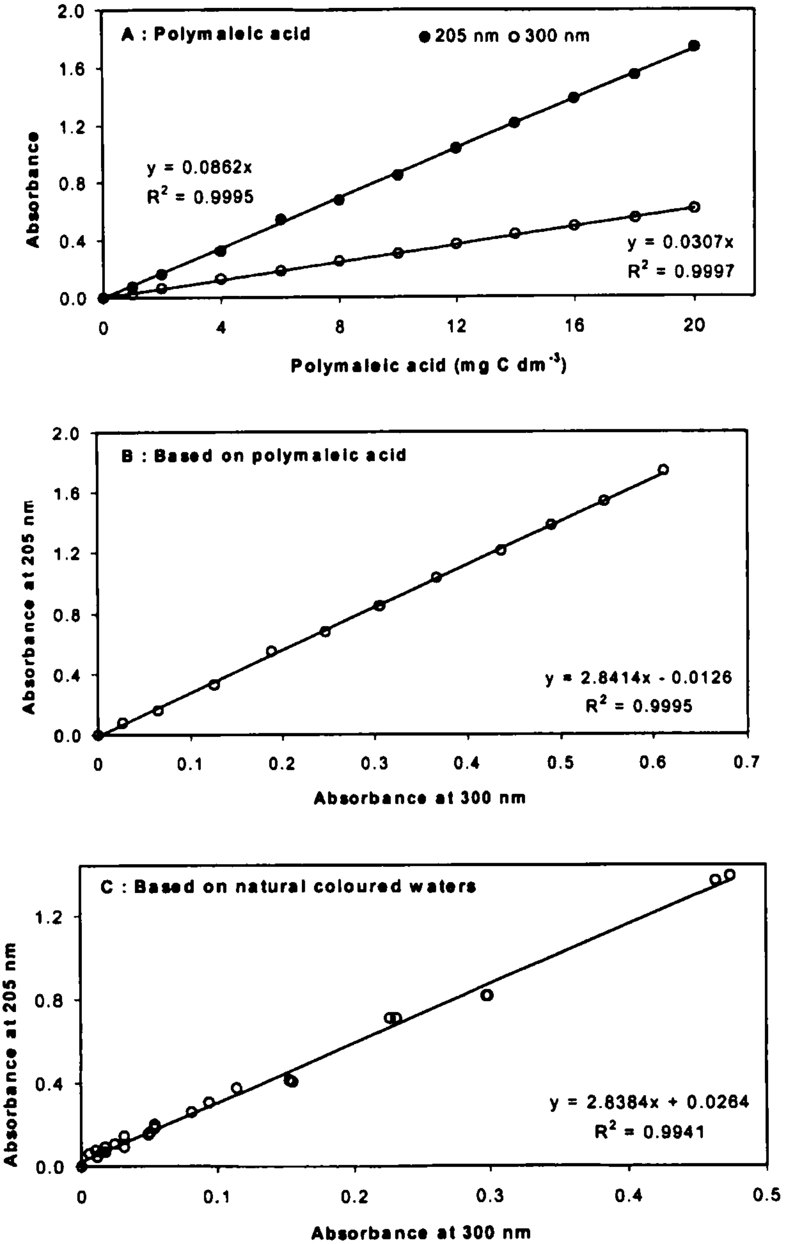

FIGURE 3 (a) Relationships between polymaleic acid concentration and UV absorption at two wavelengths, (b) a relationship between UV absorption at 205 nm and 300 nm by polymaleic acid and (c) by nitrate-free naturally colored waters using Equation-1. The net absorbance at 205 nm was then used in a traditional standard curve equation to calculate the nitrate concentration. The recovery of nitrate, based on three replicates for each treatment, varied from a minimum of 99.4% to a maximum of 103.9%, with an overall mean recovery of 100.6% (Table I). These nitrate recovery figures are well within errors in any analytical method used for nitrate analysis[11,12]. It is worth noting that the recovery figures are not particularly affected by the concentration of organic matter in the solutions.

TABLE I Recovery of nitrate from nitrate standard solutions spiked with varying amounts of polymaleic acid

Nitrate standard (mg N dm^{-3})	*Polymaleic acid concentration (mg C dm^{-3})*						*Mean*	*% RSD*	*% Recovery*
	0	*2*	*4*	*8*	*12*	*20*			
0.10	0.096	0.105	0.101	0.101	0.103	0.095	0.100	3.00	100.7
0.25	0.263	0.263	0.256	0.257	0.254	0.264	0.259	1.54	103.9
0.50	0.485	0.501	0.497	0.493	0.500	0.504	0.497	1.20	99.4
1.0	0.983	1.012	1.014	1.013	0.995	1.008	1.004	1.19	100.4
2.0	2.016	2.017	2.006	2.014	2.009	2.003	2.011	0.25	100.5
3.0	3.035	2.990	3.009	3.018	3.013	2.985	3.008	0.59	100.3
4.0	3.97	3.982	3.997	3.978	3.982	NC	3.982	0.27	99.5

NC, not calculated, because the combined (nitrate + polymaleic acid) absorbance was more than the instrumental maximum, i.e. 3.0.

Beer's law and method appraisal

The relationship between absorbance and nitrate concentration is linear up to 4 mg NO_3- N dm^{-3} when no organic matter is present. When organic matter is present, the linearity limit will be lower than this value – depending on the concentration of organic matter. In the method published by the American Public Health Association[8], the nitrate calibration curve is reported to follow Beer's law up to 11 mg NO_3-N dm^{-3} – but they chose a much less sensitive wavelength (220 nm). Therefore, it would be logical to choose a sensitive wavelength (e.g. 205 nm) for low nitrate concentration waters and a less sensitive wavelength (e.g. 210 or 220 nm) for nitrate concentrations larger than 4 mg NO_3-N dm^{-3}.

The precision of the method for the UV spectrophotometer used was evaluated by making 15 measurements on each of the following nitrate standard solutions: 0.0, 0.5, 1.0, 2.0 and 4.0 mg NO_3-N dm^{-3}. The relative standard deviation (RSD) varied from 7% for the 0.5 mg NO_3-N dm^{-3} to 0.9% for the 4 mg NO_3-N dm^{-3}. The blank (de-mineralised water) had a RSD of 74%. Relative standard deviation decreases as the concentration of an analyte increases, and blanks are known to give such a large RSD. The minimum concentration of nitrate that can be detected with the proposed UV method is dependent on the spectrophotometer and on the operational parameters (e.g. wavelength, absorbance range, and optical path length). The detection limit of the spectrophotometer used in this study was 0.045 mg NO_3-N dm^{-3}, and the minimum concentration that can be determined (determination limit) was 0.081 mg NO_3-N dm^{-3}. It should be stressed here that these precision parameters (reproducibility, detection and determination limits) will vary from one instrument to another.

The two-wavelength based method evaluated in this study was compared with the hydrazine-reduction method by analysing nitrate-N in 50 surface waters, collected from various upland streams and rivers[13]. The waters differ widely in terms of their conductivity, pH and concentrations of DOC and nitrate-N (Table II). The comparison showed that the UV spectrometry method and the reference method are in good agreement, with a regression coefficient of 0.990 (Figure 4). However, overall the UV spectrometry method overestimated the nitrate concentrations by 3.2% (slope = 0.967) when compared with the hydrazine-reduction method (Figure 4). For majority of the waters, the nitrate concentrations determined by the two methods were within ± 2%, as indicated by the descriptive statistics (Table II). The discrepancy arose mainly from three waters with below average DOC and average nitrate concentrations (Table II); the new method overestimated their nitrate-N concentrations by about 20%. The nature of the organic matter in these three waters probably caused the deviation in their ultraviolet absorption spectra, as the pH and conductivity of all samples were well within the tested ranges. Edwards and Cresser[14] found substantial deviations in linear regression relating total organic carbon and UV absorbance, which they attributed mainly to the variation in the nature of dissolved organic matter. Compared to the reference method, the UV method underestimated nitrate in five waters with above average DOC (Table II) and very low nitrate concentrations (<0.1 mg NO_3-N dm^{-3}). This is, however, mainly due to the nitrate concentrations being below or near to the determination limit of 0.08-mg NO_3-N dm^{-3} of the equipment used. Nevertheless, given the variety of water sample analysed (Table II), potential variations in the nature of organic matter, and a combination of very low nitrate and high DOC in some samples, the observed discrepancy is not unreasonable. Organic-rich upland waters in the British Isles are often very low in nitrate[15]. The UV method may not be particularly suitable for such waters, especially if the nitrate concentrations are <0.1 mg NO_3-N dm^{-3}. On the other hand, the method should have no uncertainty in the determination of nitrate in lowland waters, as they generally have nitrate concentrations ≥ 0.1 mg NO_3-N dm^{-3} and much low DOC.

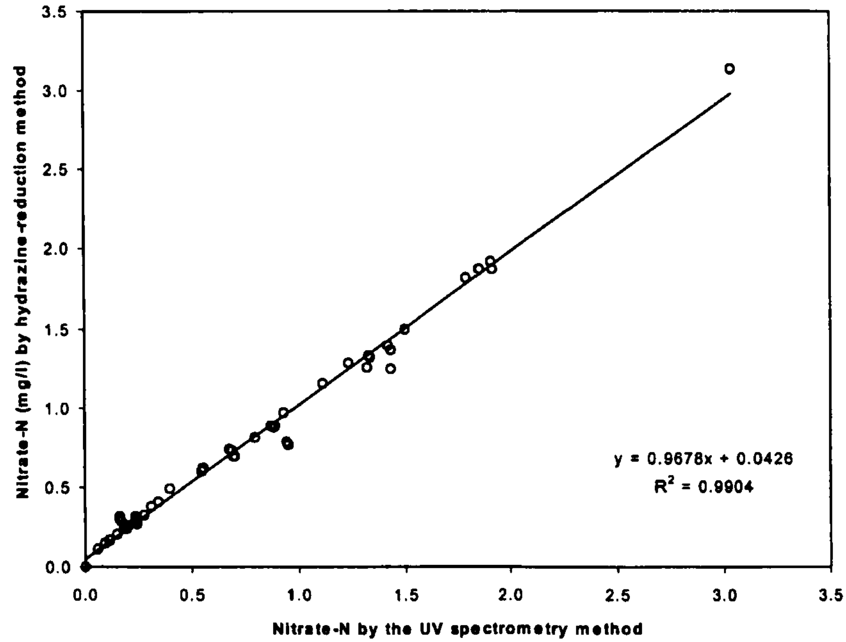

FIGURE 4 Comparison of nitrate determination by the hydrazine-reduction and a two-wavelength approach based UV spectrometry method

TABLE II DOC (mg C dm^{-3}), conductivity (μS cm^{-1}), pH and nitrate (mg N dm^{-3}) in 50 natural water samples collected from various upland and lowland locations in the UK

	DOC	*Conductivity*	*pH*	*Nitrate-N*[1]	*Nitrate-N*[2]
Mean	6.34	98.81	6.42	0.75	0.74
Standard deviation	5.20	84.36	1.06	0.65	0.66
Minimum	1.05	26.22	4.37	<0.045[3]	<0.05[4]
Maximum	20.98	535	8.24	3.14	3.04

1 and 2, determined by the hydrazine-reduction method and the spectrometry method respectively, and 3 and 4 detection limits for 1 and 2 respectively.

CONCLUSIONS

A two-wavelength approach based UV spectrometry method for the determination of nitrate in natural waters containing various amounts of dissolved organic substances was developed and evaluated. Greenberg et al.[8] also suggested a similar method for the determination of nitrate. They used a less sensitive wavelength and suggested that the empirical correction, which is dependent on the nature and concentration of organic matter, may vary from one type of water to another. However, the method reported in this paper clearly showed that the two-wavelength approach method compares reasonably well with a reference method for the determination of nitrate in a large number of different waters. The method is simple and highly reproducible and does not require any sample treatment or reagents, and will be suitable for monitoring nitrate concentrations in water bodies with varying amounts of dissolved organic matter (up to 20-mg organic carbon dm^{-3}). Nitrate determination by direct measurement of ultraviolet light absorption described in this study represents a rapid laboratory method that is low-cost and can be used in routine analysis. It should be possible to automate this method, for on-line laboratory analysis and possibly for in situ field monitoring, using modem programmable spectrophotometers.

Acknowledgements

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