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Direct determination of nitrate in natural water by ultraviolet first derivative spectrophotometry

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ABSTRACT

A simple and sensitive method for nitrate determination by ultraviolet first-derivative spectrophotometry was described. The method allows to avoid the use of sulfamic acid, routinely needed to eliminate nitrite interference, and does not require any treatment of samples except acidification. The method gives a linear calibration curve over the range 0.1-1.8 mg.L^{-1}. NO_3^- – N with a reproducibility (RSD) of 1.27 % and a limit of detection of 0.03 mg.L^{-1}. NO_3^- – N. The method is applied to determine nitrate in the ground and surface water. The comparison of results with those obtained by a reference method shows a good agreement (r = 0.9998) adequate for accurate and rapid analysis of a large number of samples.

KEYWORDS

Nitrate determination;
First-derivative spectrophotometry;
Ultraviolet spectrophotometry;
Natural water.

INTRODUCTION

In the aquatic environment, the most common ionic forms of inorganic nitrogen are ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-)[1]. These three nitrogen compounds are present in natural water as normal biological degradation products of proteins and nucleic acids, but also they can enter aquatic ecosystem via agricultural runoff, industrial wastes and sewage effluents[1,2]. Ammonia is usually oxidized to nitrite in a two step process NH_3 ou $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ by two different groups of aerobic chemoautotrophic bacteria[2,3]. Consequently the concentration of nitrate in natural water is higher than those of ammonium and nitrite[1,2]. However, nitrate in drinking water should not exceed the level of 50 mg per litre referring to the world health organization[4]. The main risk of nitrate is due to its reduction to nitrite, and subsequently to the possible occurrence of methaemoglobinaemia among bottle-fed infant below the age of six months[5] and even among children aged between 1 and 7 years[6]. In this situation, normal haemoglobin is oxidized and converted to methaemoglobin, which is incapable of binding and carrying oxygen[1,5,7]. Other possible outcomes of nitrate can take place such as cancers via the bacterial production of N-nitroso compounds, central nervous system birth defect, hypertension, diabetes, respiratory tract infection and change to the immune system, but these infectious outcomes are currently inconclusive[8]. On the one hand, the nitrate has also a direct impact to the environment, that a large input of nitrogen can cause an excessive phytoplankton and the subsequent death and decay of many aquatic organisms which unbalance the ecosystem equilibrium[1,9,10]. The determination of ni-

trate has carried out by several methods, however the most widely accepted included cadmium reduction and chromatography[11-13]. The cadmium reduction is based on reduction of nitrate to nitrite by passing the sample through a column of copperized cadmium metal filings. Nitrite are determined by a colorimetric method based on the formation of a pink-colored azo dye derived from diazotizing nitrite with sulphanilamide and coupling with N-1-naphthylethylenediamine hydrochloride (NED)[14-17]. The cadmium-reduction technique requires specialized glass columns as well as a considerable expertise to prepare a cadmium column that can maintain a satisfactory efficiency for nitrate reduction[15]. This technique leads to hazardous cadmium and phenol waste[18] and suffers from potential interferences of metal ions and phosphate[19]. Ion chromatography permits to avoid the use of hazardous reagents and has the advantages of measuring several additional anions in a single aliquot of sample. However, ion chromatography is expensive and the instrument requires frequent maintenance to function properly[18,11]. On the other hand and with a large application range than those previous techniques, nitrate selective electrodes are more and more used, yet they are less accurate and reproducible because of interferences due to several ions that occur in natural waters[18]. Other current procedures involve either nitration of phenolic compound or oxidation of a suitable reagent, in a highly concentrated sulphuric acid medium. In the case of nitration, the nitro-compound followed is either transferred in alkaline medium and subsequently measured by colorimetry as the yellow nitro-phenolate[14,20-26], or directly measured by polarography through a reduction on mercury electrode[27]. In the second case, the oxidation of a suitable reagent can be done either by nitrite coming from nitrate reduction through a copperised cadmium column[28-31] or directly by nitrate[32-35] and both way yield to colored reaction product, which can colorimetrically determined. However, the most common of these procedures are complicated, waste of time, producing hazardous waste, they are subjects of many interferences and have firmly accuracy depended on reaction conditions. The strong absorbance of nitrate ion in ultraviolet range near 203 nm[36] has been investigated for early time for determination of nitrate in natural water[37,38]. The method is simple, rapid and requires no chemical reagents except KNO_3 and diluted acid needed for preparing standard solutions[39]. However, many interferences especially due to chloride and organic matter, limit the use of this method for many kinds of natural water. In general, the determination of nitrate by direct measurement in ultraviolet range can not be accurate and selective without separating nitrate from foreign species as described by some previous works[40-44]. In recent years, derivative spectrophotometer has received an increasing attention and becomes a practical analytical method. It represents another way to determine nitrate in water independently of the most interferences and without having the use of hazardous chemicals or applying a complicated procedures. Simal et al[45] were used second derivative spectrophotometry to determine nitrate at 224 nm, however at this wave length, NO_2^- has a second-derivative signature very similar to that of NO_3^-[45,11] and the method requires sulfamic acid to remove NO_2^- as nitrogen. Another way to avoid the interference of NO_2^- is to measure with less resolution the second-derivative absorbance of NO_3^- at the zero crossing point of NO_2^- as described by Suzuki et al[46]. First derivative ultraviolet spectrophotometry seems also an accurate and reproducible method, however it has never been used for determination nitrate in water. So for this reason the main purpose of this work is to investigate this method in order to reduce mostly the previous interferences and to prevent the application of sample pre-treatment. The determination of nitrate has been carried out by measuring the first-derivative absorbance at the zero crossing point of nitrite. It was observed that no significant interferences were recorded in the presence of the most foreign species which could be found in natural water, and for a wide variety of samples, results with the proposed method are in good agreement with those obtained by the sodium salicylate method[14,26]. The main advantages of the proposed method are simple, rapid, accurate and requires no sample pre-treatment which makes it useful for routine analysis of large number of samples.

EXPERIMENTAL

Apparatus

Spectroscopic measurements were performed us-

ing a double beam Shimadzu UV-2401PC model recording UV-VIS spectrophotometer. The apparatus is interfaced to an IBM-PC computer which is used to record spectra and calculate derivative from absorbance. The scanning range runs from 1100 to 190 nm and derivatives absorbance versus wavelength are calculated by least square procedure in basing on a convolution functions.

Operating conditions

Direct absorbance spectra were obtained from scans of standards and samples between 250 and 190 nm with matched pairs of UV quartz cell with 1 cm optical path lengths. Automatic adjustable deuterium lamp was used and all scans are conducted at high speed (190 nm/min) against a reference of double distilled water. The slit width is fixed at 0.1 nm and sampling interval is chosen automatically. First derivative spectra are obtained with a sampling interval of 1nm and they are multiplied by 10 scaling factor.

Reagents, standards and samples

All used chemicals were of analytical reagent grade and double distilled water was used in all preparation. Standard stock solution containing 100 $mg.L^{-1}$. NO_3^- – N was prepared by dissolving accurately 0.1805 g of KNO_3 after drying at 105°C for 4 hours, in 250 ml of water. The stock solution was stored in a refrigerator at 4°C and refreshed after each three months. Working standards ranging from 0.1 to 1.8 $mg.L^{-1}$ NO_3^- – N were prepared immediately before usage from serial dilution of stock solution. Other solutions used for the interference study were prepared by dissolving the corresponding salt in water. Ground and surface water samples were collected in polyethylene vessels and mineral water samples were purchased from local market. Samples were filtered through 40 grade Whatman filter paper.

RESULTS AND DISCUSSION

Interferences in direct determination in UV

The ion nitrate absorbs strongly in the UV range with a maximum absorbance at 203 nm and molar absorptivity was estimated as 8800 $L.mol^{-1}.cm^{-1}$. However nitrate determination based on direct spectrophotometry measurement in ultraviolet is usually hindered by the presence of other absorbing species such as Cl^-, NO_2^-, Fe^{3+} and organic matter[47]. Figure 1 shows these interferences in which nitrate spectrum is superposed with those of foreign species. Nitrate is expressed as nitrate nitrogen and concentration of 1 $mg.L^{-1}$. NO_3^- – N will be used in all the following interference studies in this paper. It has been observed that nitrite is the most interfering species, that with an equal amount, nitrite has almost the half absorbance at 203 nm than of nitrate, and both ions give overlapping absorption bands, which makes their visual identification difficult. For this reason, direct determination in UV range usually require pre-treatment of sample such as nitrate separation by ion-exchange chromatography[43,47] or by dialysis membrane[41].

First derivative determination

The purpose of using first derivative spectrophotometry is to find a wave length in the UV range in which only nitrate absorbs and other species do not, or slightly absorb. The zero-crossing point of nitrite near 209.50 nm seems to be the desired wave length in which nitrate absorbs significantly and neither chloride nor bicarbonate (HCO_3^-) and iron (Fe^{3+}) absorb (Figure 2). Spectra of some standard solutions which have been used to determine calibration curve, as well as their first derivative are presented in Figure 3. Calibration curve plotting first-derivative absorbance of nitrate at 209.50 nm versus concentration, shows a linear relationship from 0 to 2.4 $mg.L^{-1}$ NO_3^- – N, but a strong correlation (r = 0.9997) has been noticed below 1.8 $mg.L^{-1}$ NO_3^- – N as it is showed in Figure 4. So for this reason all samples were enough diluted by water to make their nitrate concentration under this level and the linear range between 0 and 1.8 $mg.L^{-1}$ NO_3^- – N will be used for all next determinations.

(a) Interference of foreign species

It has been noticed that the zero-crossing point of nitrite can undergo a small shift when its concentration varies to the high values. Consequently, the interference of nitrite was studied in using mixtures of fixed amount of nitrate and a variable amount of nitrite until the two ions reach an equal quantity. Five replicated determination was carried out for each mixture by measuring the first derivative absorbance at 209.50 nm. As it is shown in TABLE 1, it has been found that for all the mixtures the

reproducibility (relative standard deviation) is below 2% and recovery did not exceed 2.5% around the value of 100 %. The same work was done with chloride, the second serious interfering species, by mixing 1 mg.L^{-1}. NO_3^- – N with variable amount of chloride and the first-derivative absorbance was measured at 209.50 nm.

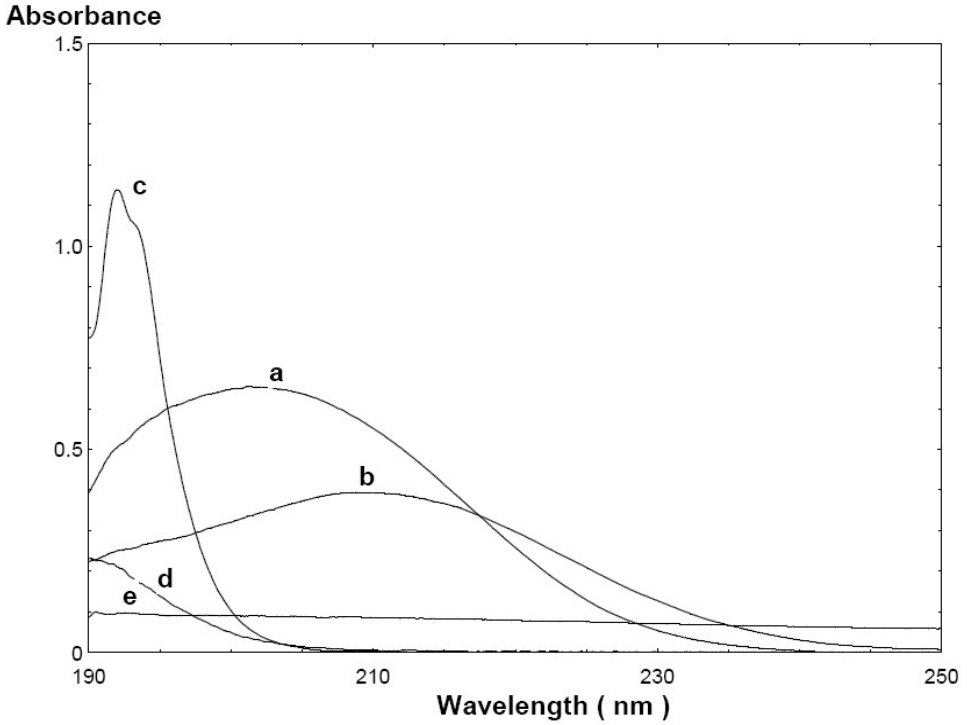

Figure 1 : Interference on nitrate determination in UV range; a: 1 mg.L^{-1} NO_3^- – N, b: 1 mg.L^{-1} NO_2^- – N, c: 200 mg.L^{-1} chloride, d: 100 mg.L^{-1} HCO_3^-, e: 1 mg.L^{-1} iron (III).

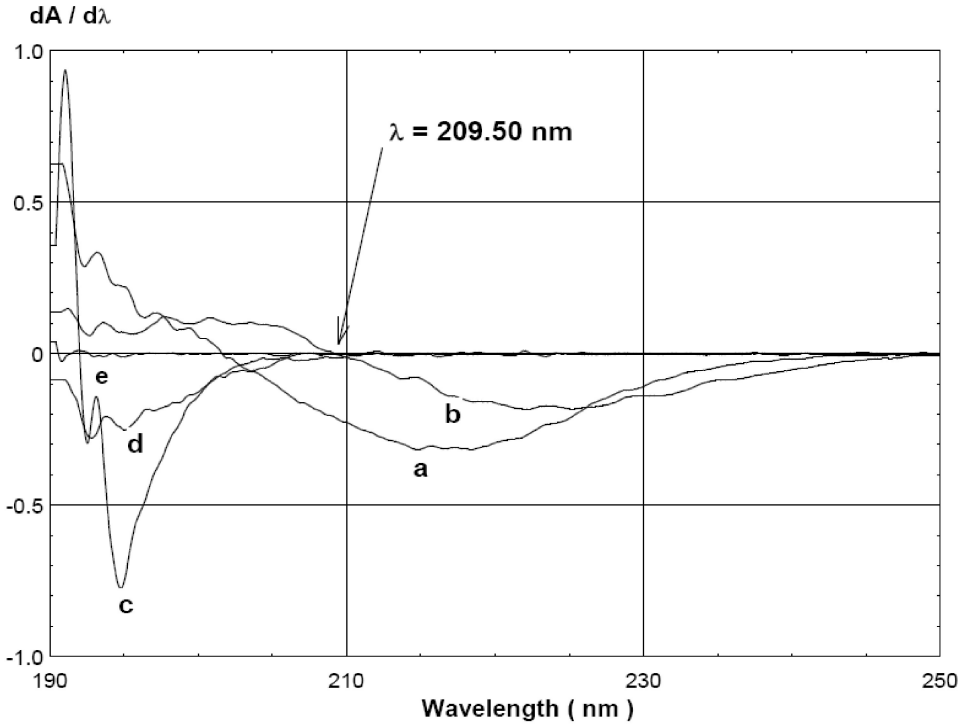

Figure 2 : First derivative spectra of nitrate and some of others species; a: 1 mg.L^{-1} NO_3^- – N, b: 1 mg.L^{-1} NO_2^- – N, c: 200 mg.L^{-1} chloride, d: 100 mg.L^{-1} HCO_3^-, e: 1 mg.L^{-1} iron (III).

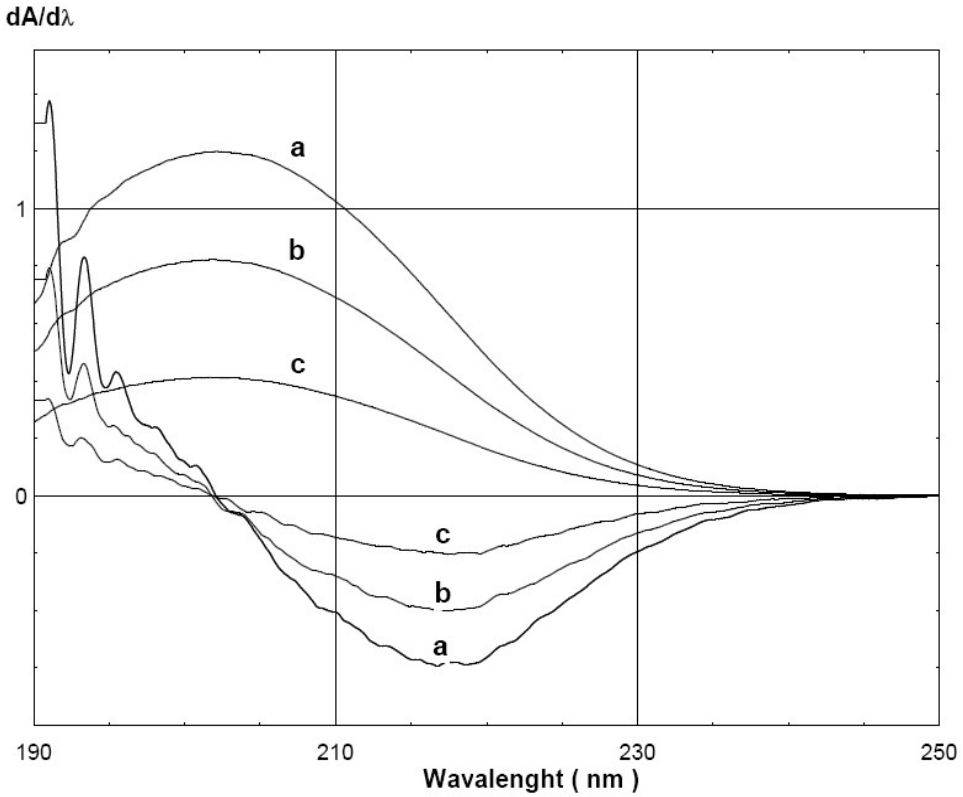

Figure 3 : Zero and first-order derivative spectra of some standard solutions; a : 1.8 mg.L^{-1} NO_3^- – N, b: 1.2 mg.L^{-1} NO_3^- – N, c: 0.6 mg.L^{-1} NO_3^- – N.

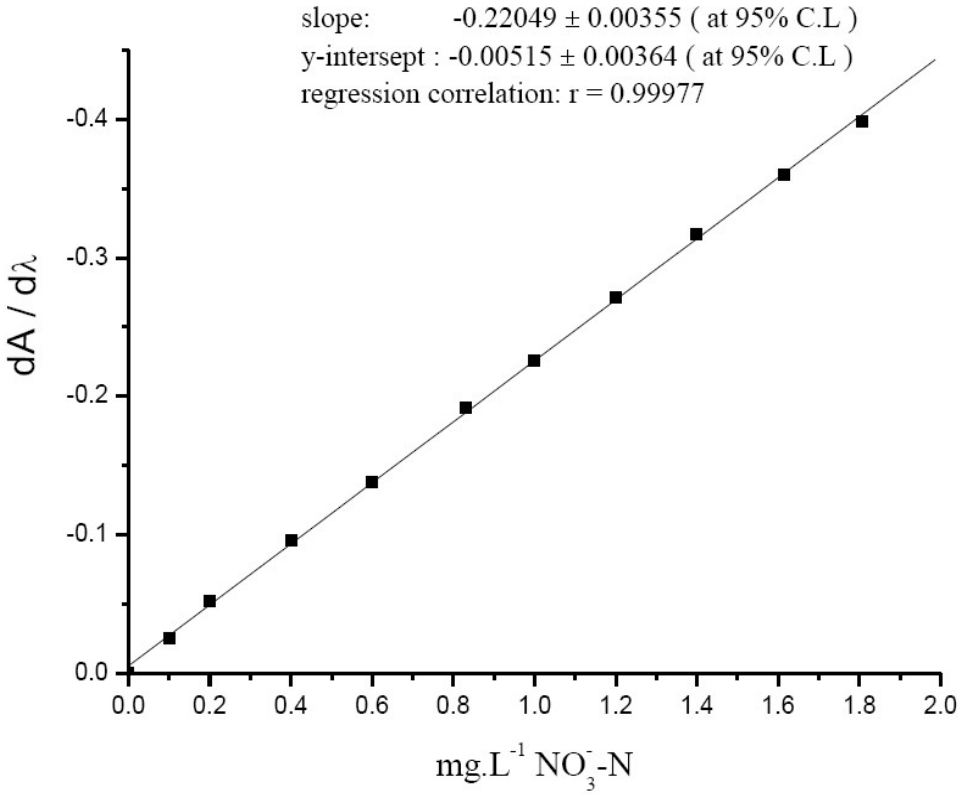

Figure 4 : Calibration curve obtained with first-derivative technique from standards ranging from 0.0 to 1.8 mg.L^{-1} NO_3^- – N. The curve was fitted by least-squares regression (r = 0.99977)

The TABLE 2 shows that the chloride do not interfere in a meaningful manner only from 1000 mg.L^{-1} while introducing an error of 5 %. This observation shows that the method tolerates high concentrations of chlorides and will be well adequate for the most types of natural waters. Bicarbonate does not interfere at the concentration which is less than 100 mg.L^{-1} introducing only a small error of 0.9 % (TABLE 3) on the nitrate determination.

TABLE 1 : Interference of nitrite on the determination of 1 mg.L^{-1}. NO_3^- – N

NO_3-N added (mg.L^{-1})	NO_2-N added (mg.L^{-1})	NO_3-N found[(a)] (mg.L^{-1})	RSD (%)	Recovery (%)
1	0	1.004	0.98	100.4
1	0.2	1.019	1.44	101.9
1	0.4	1.024	0.88	102.4
1	0.6	1.016	1.44	101.6
1	0.8	0.984	0.99	98.4
1	1	0.997	0.82	99.7

[(a)]**The average of five replicate determinations (n = 5)**

TABLE 2 : Interference of chloride on the determination of 1 mg.L^{-1}. NO_3^- – N

Chloride (mg.L^{-1})	N-NO_3 found[(a)] (mg.L^{-1})	RSD (%)	Recovery (%)
100	1.010	1.33	101.0
200	1.013	0.79	101.3
300	1.011	0.90	101.1
400	1.019	0.74	101.9
500	1.030	1.79	103.0
600	1.037	1.98	103.7
700	1.032	1.82	103.2
800	1.035	1.21	103.5
900	1.042	0.82	104.2
1000	1.049	1.13	104.9
1200	1.082	0.88	108.2
1500	1.101	0.80	110.1
1700	1.100	0.95	110.0
2000	1.123	1.31	112.3

[(a)]**The average of five replicate determinations (n = 5).**

However according to the method of nitrate determination by second-derivative spectrophotometry, Simal et al[45] are reported an interference of HCO_3^- at concentration since 0.5 mg.L^{-1}, and recommended acidification under pH = 2 to eliminate this interference. In the present procedure, the acidification is involved only when concentration of HCO_3^- reach 200 mg.L^{-1} (TABLE 3). Furthermore it has been found that for the most types of natural water the addition of 1 ml of *1N*, H_2SO_4 for each 50 ml of sample can maintain the pH value under 2.5, which yield to eliminate bicarbonate interference. TABLE 4 shows a quantitative recovery on the nitrate determination after acidification, even if the initial concentration of HCO_3^- was 700 mg.L^{-1}. The influence of other foreign species that are commonly found in natural water was investigated, and the amount at which the species cause an error of more than 5 % is taken as its limited tolerance. The results of TABLE 5 show that large amount of alkaline earth metal such as calcium and magnesium is tolerable by the proposed method for up to 200 mg.L^{-1} and that of orthophosphate is tolerated for up to 100 mg.L^{-1}. Moreover, glucose and humic acid does not interfere even at 1000 and 300 mg.L^{-1} respectively, showing a good robustness of the method in the presence of organic matter.

TABLE 3 : Interferences of bicarbonate on the determination of 1 mg.L^{-1}. NO_3^- – N

Bicarbonate added (mg.L^{-1})	N-NO_3 found (mg.L^{-1})[(a)]	RSD (%)	Recovry (%)
100	1.009	0.96	101.9
200	1.047	0.62	104.7
300	1.091	0.76	109.1
400	1.172	1.21	117.2
500	1.225	0.91	122.5
600	1.237	0.99	123.7
700	1.298	1.33	129.8

[(a)]**The average of five replicate determinations (n = 5).**

TABLE 4 : Interferences of bicarbonate on the determination of 1 mg.L^{-1}. NO_3^- – N after acidification by H_2SO_4

Bicarbonate added (mg.L^{-1})	N-NO_3 found (mg.L^{-1})[(a)]	RSD (%)	Recovry (%)
200	0.999	0.75	99.9
300	1.002	1.41	100.2
400	1.006	0.98	100.6
500	0.989	0.78	98.9
600	0.997	0.94	99.7
700	1.000	1.98	100.0

[(a)]**The average of five replicate determinations (n = 5).**

It has been also found (TABLE 6) that some heavy metal such as iron and zinc are tolerable at mass ratio NO_3^- – N/interferent of 1:5 and 1:20 respectively, how-

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ever the amount of lead, copper and chromium hexavalent should not exceed the mass ration NO_3^- – N/ interferent of 1:2 when a quantitative nitrate determination is required.

TABLE 5 : Interferences of alkaline earth and some currently species on the determination of 1 mg.L^{-1}. NO_3^- – N

Species	Mass ratio N-NO_3/ Interferent	Recovery (%)[a]	RSD (%)
Ca^{2+}	1 :100	100.6	1.02
	1 :200	101.0	0.98
Mg^{2+}	1:100	100.4	0.78
	1 :200	99.3	1.73
PO_4^{3-} (added as Na_3PO_4)	1 :10	100.3	1.34
	1 :70	100.4	0.42
	1 :100	100.1	0.70
NH_4^+	1 :5	100.2	1.30
	1 :10	101.0	0.71
SO_4^{2-}	1 :100	101.1	1.62
	1 :200	98.8	1.27
Glucose	1 :100	100.0	0.63
	1 :300	100.1	0.41
	1 :500	100.3	1.50
	1 :1000	101.0	1.18
Humic acid	1 :100	100.1	0.97
	1 :200	100.2	0.99
	1 :300	101.0	1.14

[a]The average of five replicate determinations (n = 5)

(b) Evaluation of the method

The performance of the method was evaluated in term of linear range, detection limit and reproducibility (TABLE 7). The calibration curve was linear in the range 0.10-1.8 mg.L^{-1} NO_3^- – N with a correlation coefficient of 0.9997. The detection limit was defined as the concentration equivalent of three times the standard deviation of the blank divided by the slope of the calibration curve[48]. For 25 measurements of the blank, the detection limit was:

3σ/(slope of the calibration curve) = 0.03 mg.L^{-1} NO_3^- – N, as well as the determination limit was : 10σ / (slope of the calibration curve) = 0.10 mg.L^{-1} NO_3^- – N. The reproducibility (RSD) of the method was 1.27 % performed by ten separate determinations of 1 mg.L^{-1}.

TABLE 6 : Interferences of heavy metals on the determination of 1 mg.L^{-1}. NO_3^- – N

Species	Mass ratio N-NO_3/ Interferent	Recovery (%)[a]	RSD (%)
Fe^{2+}	1 :2	99.9	0.57
	1 :5	99.0	0.73
	1 :10	96.9	0.81
Fe^{3+}	1 :2	99.5	0.96
	1 :5	96.9	1.37
	1 :10	89.9	2.09
Zn^{2+}	1 :2	99.3	1.11
	1 :5	98.7	0.64
	1 :20	100.5	0.71
Cu^{2+}	1 :2	101.4	0.69
	1 :5	115.0	0.10
	1 :20	154.9	1.35
Pb^{2+}	1 :1	98.6	1.31
	1 :2	94.9	6.84
	1 :5	93.4	1.82
Cr^{3+}	1 :2	102.5	0.69
Cr^{6+}	1 :2	135.0	0.96
Ag^+	1 :2	96.5	0.90
Co^{2+}	1 :2	101.7	0.96
Ni^{2+}	1 :2	102.2	1.25

[a]The average of five replicate determinations (n = 5)

NO_3^- – N. The previous results show that the proposed method is more accurate and can tolerate the presence of many interfering species than second-derivative method which is described by simal et al[45] and later by suzuki et al[46].

(c) Application to real samples

The method was applied to determine the nitrate in certain samples such as tape water, mineral water, river and lake water and ground water. Except the mineral water, all samples are filtered through 40 grade whatman filter (<0.8 μm) prior to analysis and acidified by 1 ml of *1N*, H_2SO_4 for each final volume of 50 ml of diluted sample. TABLE 8 shows a good agreement between results obtained by the proposed method and those obtained by sodium salicylate method which commonly accepted as a reference method for nitrate determination[49]. Analysis by least square regression showed a very strong relationship (r = 0.9998) between the tow methods (Figure 5). The slope of the best-fit regression

TABLE 7 : Analytical figure of merit for the determination of nitrate as nitrogen by the proposed method

Linear range (mg.L^{-1}. NO_3^- – N)	:	0.10 – 1.8
Slope of the calibration curve	:	-0.22049 ± 0.00355 (at 95 % confidence level)
Y – intercept	:	-0.00515 ± 0.00364 (at 95 % confidence level)
Correlation coefficient	:	r = 0.9997
Limit of detection (mg.L^{-1}. NO_3^- – N)	:	0.03
Limit of determination (mg.L^{-1}. NO_3^- – N)	:	0.10
Reproducibility (% RSD)	:	1.27
Blank measurement (n = 25)	:	-0.00106 ± 0.00225

line (at 95 % confidence level) was 1.00269 (± 0.01190) and the y-intercept (at 95 % confidence level) was 0.01680 (± 0.25190) mg.L^{-1}. A paired-sample t-test gives as results (n = 15, mean difference = 0.03, SD = 0.304, t = 0.3822) demonstrating that there was no significant difference between NO_3^- – N concentrations obtained through sodium salicylate method and ultraviolet first derivative spectrophotometry.

(d) Recommended procedure

First of all, a direct measurement in the ultraviolet range should be done, and if the nitrate absorption at 203 nm is above the value 1.2, the sample will be enough diluted in order to make its absorption into the first-derivative linear range. Second, 1 ml of 1N, H_2SO_4 is added to each final volume of 50 ml of diluted sample, and first derivative absorption is recorded at 209.50 nm in using the same operating conditions that is described in an experimental section. The unknown concentration is determined by projecting the first-derivative absorption of the sample on the calibration curve plotted by standard solutions ranging from 0.1 to 1.8 mg.L^{-1} NO_3^- – N. The use of the proposed method is limited by a mass ratio NO_3^- – N / chloride above 1:1000. In this case, the sample should be treated before the analysis by an equivalent quantity of $AgSO_4$.

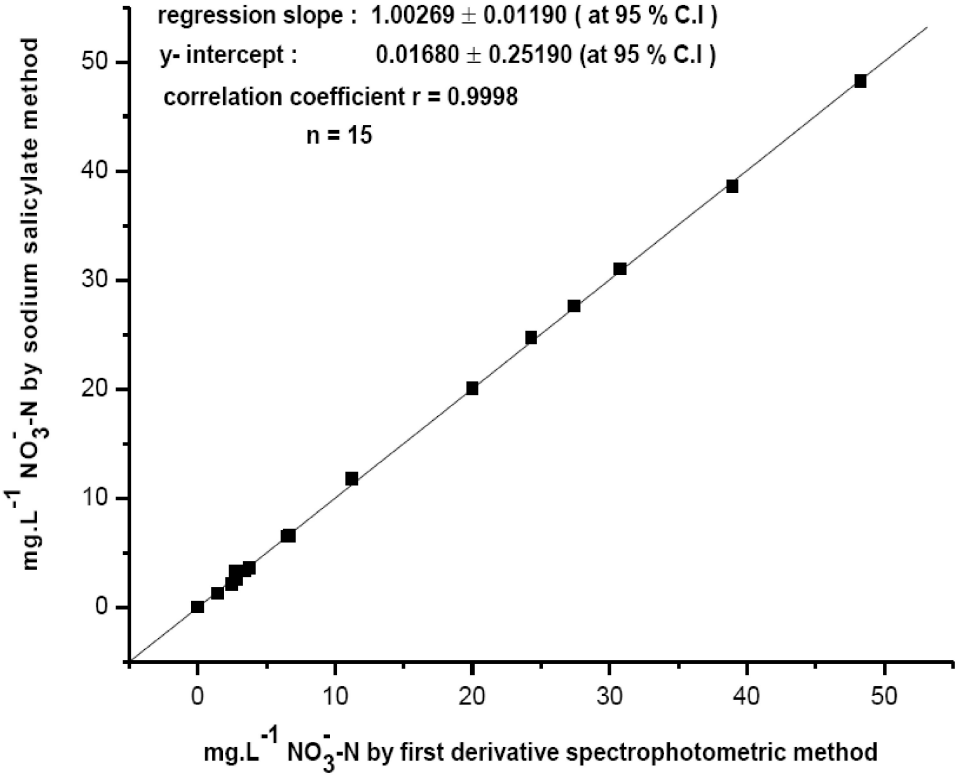

Figure 5 : Comparison of NO_3^- – N concentration for 15 natural waters samples as determined by first-derivative spectrophotometry and by sodium salicylate method.

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TABLE 8 : Determination of nitrate in real samples and comparison with reference method

Sample type	NO_3-N added ($mg.L^{-1}$)	UV first-derivative method[a] ($mg.L^{-1}$)	Sodium salicylate method ($mg.L^{-1}$)	RSD (%)	Recovery (%)
Tap water	-	2.48	2.12	1.17	
	5	7.42		1.70	98.9
Well 1 (sidi jaber, Fahs, Zaghouan)	-	3.44	3.37	1.60	
	5	8.43		1.25	99.8
Well 2 (ksar hellal, Monastir)	-	24.30	24.73	1.20	
	10	34.00		0.61	97.7
Well 3 (Mornaguia, Manouba)	-	48.30	48.21	0.90	
	20	68.70		0.64	102.0
Well 4 (Chbika, Kairouan)	-	6.67	6.54	0.96	
	10	16.69		1.28	100.2
Mineral water 1 (Safia, Ksour ®)	-	3.79	3.61	1.98	
	2	5.82		0.87	101.5
Mineral water 2 (Cristalline ®)	-	1.49	1.30	0.96	
	4	5.60		1.32	102.7
Mineral water 3 (Fourate ®)	-	2.82	2.58	0.64	
	2	4.84		1.01	101.0
Lake water (Fjije, Fahs, Zaghouan)	-	0.53	0.21	2.07	
	2	2.57		1.22	101.9
River water 1 (Malyen, Fahs, Zaghouan)	-	0.75	1.50	1.57	
	2	2.80		0.72	102.8
River water 2 (Bir mcharga, Zaghouan)	-	1.59	0.95	0.98	
	2.5	4.13		1.00	101.6

[a]**The average of five replicate determinations (n = 5)**

CONCLUSION

The proposed method shows a good accuracy and reproducibility in the presence of several interfering species and for many real samples. The method does not require any pre-treatment of sample except acidification, which is useful for rapid and routine analysis. The method shows competitive precision, selectivity and a comparable linear range than second-derivative spectrophotometry and sodium salicylate method, which allow it to be an alternative method for nitrate determination in natural water.

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