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Quantification of nitrite and nitrate in seawater by triethyloxonium tetrafluoroborate derivatization—Headspace SPME GC–MS

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ABSTRACT

Triethyloxonium tetrafluoroborate derivatization combined with direct headspace (HS) or SPME-gas chromatography–mass spectrometry (GC–MS) is proposed here for the simultaneous determination of nitrite and nitrate in seawater at micromolar level after conversion to their corresponding volatile ethyl-esters (EtO-NO and EtO-NO_2). Isotopically enriched nitrite [^{15}N] and nitrate [^{15}N] are employed as internal standards and for quantification purposes. HS-GC–MS provided instrumental detection limits of 0.07 μM NO_2^- and 2 μM NO_3^-. Validation of the methodology was achieved by determination of nitrite and nitrate in MOOS-1 (Seawater Certified Reference Material for Nutrients, NRC Canada), yielding results in excellent agreement with certified values. All critical aspects connected with the potential inter-conversion between nitrite and nitrate (less than 10%) were evaluated and corrected for by the use of the isotopically enriched internal standard.

1. Introduction

Nitrite and nitrate are ubiquitous and the availability of analytical methods for their simultaneous determination at trace and ultra-trace levels in complex matrices is important for understanding aspects of environmental and biological processes. They reflect the final states of a variety of N-compounds in many metabolic pathways occurring in living systems [1,2]. Issues related to their speciation in body fluids are explored in order to understand the role of NO as a regulatory molecule in the vascular system, in the brain, and in the immune system [3]. Direct determination of NO gas is a challenge for Analytical Chemistry and the use of nitrite and nitrate as NO metabolic products are exploitable for this purpose.

Environmental contamination by nitrite and nitrate can occur through industrial and domestic combustion and from agricultural sources; their monitoring has gained increasing importance [1].

The state of the art of their analytical determination has been reviewed by Moorcroft [1] and Jobgen [4] who focused their attention on liquid-phase molecular spectroscopy (determination by UV–vis and chemiluminescence) and electrochemical detection. Both techniques are often used in combination with chromatographic separation or capillary electrophoresis in order to perform on-line detection which suffers, in general, from limited selectivity and sensitivity, especially due to high matrix effects. One additional drawback is related to the derivatization step: many reactions have been proposed to convert nitrite to a suitable molecule for detection whereas little attention has been given to the less reactive nitrate, which can be only determined following a critical reduction. This separation step suffers matrix effects when real samples are processed, especially proteinaceous materials. Tsikas [5] presented an overview of currently available assays for nitrate and nitrite based on the Griess reaction.

The use of GC–MS in this field has also been proposed and recently reviewed by Helmke [3]. GC–MS strategies for the analysis of these two anions include nitration using aromatic compounds and alkylation with pentafluorobenzyl bromide (PFB-Br). The first approach is applicable only for the direct determination of nitrate ion as nitrite does not react under the specified conditions; for its detection a critical oxidation step is required. The latter approach is able to achieve simultaneous determination of both anions [6]. In any case, derivatization of nitrate ion by PFB-Br requires demanding reaction conditions such as elevated temperature and high PFB-Br concentration [3]. Tsikas [7] published the first method for the determination of nitrite by GC–MS which was free of derivatization, but it has not been used for the determination of nitrate.

Recently, analytical application of triethyloxonium tetrafluoroborate salt (TEOT) has been proposed by the authors for the chemical vapor generation (CVG) of Cl^-, Br^-, I^-, CN^-, SCN^-, S^{2-},

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NO_3^-, NO_2^- [8]. Trialkyloxonium "Meerwein" reagents [9,10] have proven capable of aqueous phase alkylation of several inorganic substrates, allowing their separation from the reaction matrix as volatile or semi-volatile reaction products of defined chemical composition [8]. The TEOT method has been validated by determination of bromide in BCR-612 reference material and has been applied to the determination of iodine and iodate [8].

TEOT converts nitrite and nitrate to their corresponding ethyl esters through an O-alkylation reaction. These molecules present suitable volatility and stability to be determined by GC–MS.

In this work we propose, for the first time, application of a CVG-GC–MS methodology for the simultaneous determination of nitrite and nitrate at micromolar level. The procedure is simple and the use of isotopically enriched internal standards confers ruggedness to the method. Validation has been achieved by analysis of a "Seawater Certified Reference Material for Nutrients", MOOS-1. Results reported here demonstrate the analytical potentialities and usefulness of aqueous phase alkylation with TEOT for the determination of anionic species by CVG.

2. Experimental

2.1. Reagents and materials

Aqueous solutions of isotopically enriched nitrite and nitrate were prepared by dissolution of sodium nitrite (^{15}N, 98%+) and potassium nitrate (^{15}N, 99%), respectively (Cambridge Isotope Laboratories, Inc.) in ultrapure water in order to obtain final concentrations of 200 mg/L $^{15}NO_3^-$ and 20 mg/L $^{15}NO_2^-$. An alkylating solution of TEOT (triethyloxonium tetrafluoroborate) was prepared by dissolving the reagent (Fluka: TEOT >97%) in ultrapure water; the quantity of solid salt required to ensure 40 mg of reactant in 100 μL solution. Aqueous oxonium salts are unstable, so the solution is prepared just prior to sample derivatization. Working solutions of nitrite and nitrate were prepared by dilution of Fluka concentrates (Fluka: nitrate, certified anion standard solution 1001 mg/L ± 2 mg/L; nitrite standard for IC 1000 mg/L ± 4 mg/L) with ultrapure water. All standard solutions were stored at 4 °C.

2.2. GC–MS methods

GC–MS experiments were performed using an Agilent GC 6850 equipped with an Agilent 5975 C MS detector. For the HS-GC–MS procedure, manual sample injection was employed using a 250 μL sample volume. The oven program consisted of the following: isothermal (10 min) at 30 °C, 5 °C/min to 100 °C maintained for 4 min, 25 °C/min to 240 °C maintained for 10 min. Inlet setup: inlet mode is pulsed split with split ratio 8:1, pulsed pressure 200 kPa and temperature 150 °C. A model J&W 122-1364E DB-624 column (6% Cyanopropyl-phenyl 94% dimethyl polysiloxane) was used in constant flow mode at 0.7 mL He/min. Mass spectrometry detection (70 eV electron impact, transfer line 260 °C, ion source 250 °C) was performed in SIM mode monitoring *m*/*z* 30–31–60–61 (dwell time 100 ms for each *m*/*z*) for nitrous acid ethyl ester and *m*/*z* 46–47–76–77 for nitric acid ethyl ester (same dwell time).

For the SPME-GC–MS procedure, a 57310-U df 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) Supelco SPME fiber assembly was used. The fiber was exposed to the headspace of the vial for 10 min at ambient temperature whereas the desorption process required 1.5 min in the GC inlet. The oven program consisted of: isothermal (10 min) at 30 °C, 10 °C/min to 80 °C, 25 °C/min to 200 °C maintained for 10 min. Inlet setup: inlet mode is pulsed split with split ratio 5:1, pulsed pressure 180 kPa and temperature 170 °C. A model J&W 122-1364E DB-624 column (6% Cyanopropyl-phenyl 94% dimethyl polysiloxane) was operated in constant flow mode at 1 mL He/min. Mass spectrometry detection (70 eV electron impact, transfer line 260 °C, ion source 250 °C) was performed in SIM mode monitoring *m*/*z* 30–31–60–61 (dwell time 100 ms for each *m*/*z*) for nitrous acid ethyl ester and *m*/*z* 46–47–76–77 for nitric acid ethyl ester (same dwell time).

2.3. Sample preparation

A 2 mL sample was introduced without any pretreatment into a 4 mL vial and isotope enriched spike (100 μL) added. After sealing, 100 μL aqueous TEOT was injected through the septum. GC–MS analysis was performed after 3 h reaction time at 23 °C; the HS procedure required the injection of 250 μL of headspace; SPME entails the exposure of the fiber in the headspace for 10 min.

3. Results and discussion

3.1. Identification

Nitrite and nitrate are converted to their corresponding ethyl esters by TEOT. TEOT is a strong alkylating agent which is able to perform alkylation in aqueous solution and to react with anions in neutral substrates. In the present case, O-alkylation of the substrate occurs with the formation of nitrous and nitric ethyl ester:

No volatile products arising from N-alkylation of nitrite and nitrate have been observed. Nitrite and nitrate ethyl esters are suitable for GC–MS analysis and their corresponding EI mass spectra are reported in Figs. 1–2. In the case of the nitrite ethyl ester (Fig. 1), we note the absence of a molecular ion and the fragmentation produced $[CH_2NO_2]^+$ ion (*m*/*z* 60) which corresponds to the loss of 15 amu (methyl loss) and the ion $[NO]^+$ (*m*/*z* 30) which corresponds to loss of 45 amu (ethoxy loss). For the nitrate ethyl ester (Fig. 2), the interpretation of the mass spectrum is similar to the nitrite ethyl ester, and the EI spectrum is the same as reported in the NIST05 library. Unfortunately, there is no possibility of making a similar comparison for the nitrite ethyl ester. Mass spectra reported in our previous work [8] were obtained using a Varian 3400CX GC equipped with a 1077 split–splitless injector directly interfaced to a Saturn3 ion trap mass spectrometer (Varian). Mass spectra presented here are obtained with a different apparatus and tune setting. As a consequence, some small differences in relative intensities of the fragment ions can be noted. With the actual settings of the MS, the mass spectra are of better quality with a view to analytical determination of nitrite and nitrate.

3.2. Quantification method and inter-conversion of nitrite and nitrate

With the proposed method, the problem arising from the potential chemical inter-conversion of nitrite and nitrate during the derivatization step has been evaluated. It has been proven that no detectable conversion of nitrate to nitrite arises whereas the conversion of nitrite to nitrate is observed and occurs to the extent of about 10% at the 0.2 mM NO_2^- concentration level. This problem likely originates with the presence of dissolved atmospheric oxygen [11,12] and the strong acidic conditions that arise from the acid hydrolysis of TEOT. This interfering effect can be corrected for by the use of the isotopically enriched internal standard.

The following equations describe the methodology used for the elaboration of the data. The algorithm proposed is similar to that

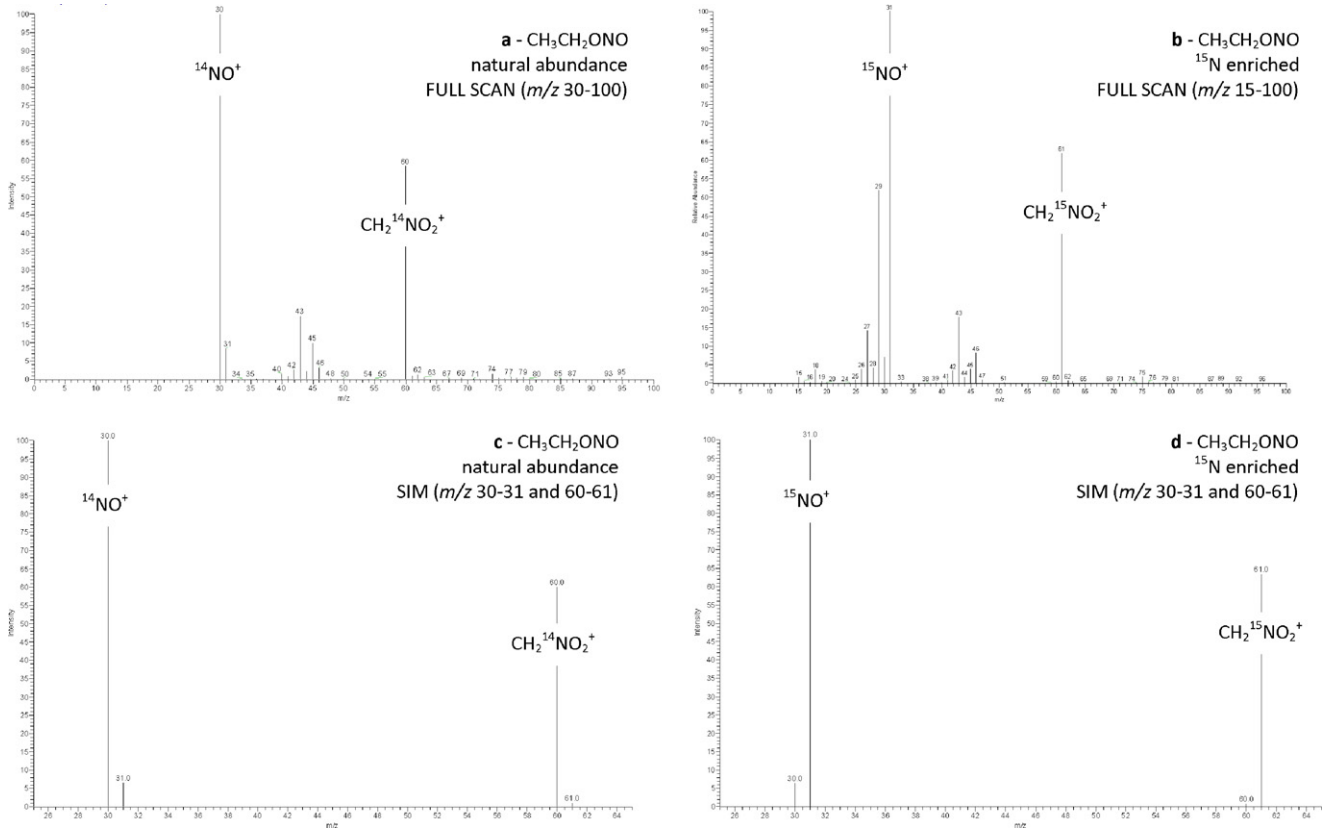

Fig. 1. Nitrous acid ethyl ester, CH_3CH_2ONO. (a) Full scan mass spectra (m/z 30–100) of the standard of natural origin. (b) Full scan mass spectra (m/z 15–100) of the ^{15}N enriched standard. (c) SIM mass spectra (m/z 30–31 and 60–61) of the standard of natural origin. (d) SIM mass spectra (m/z 30–31 and 60–61) of the ^{15}N enriched standard.

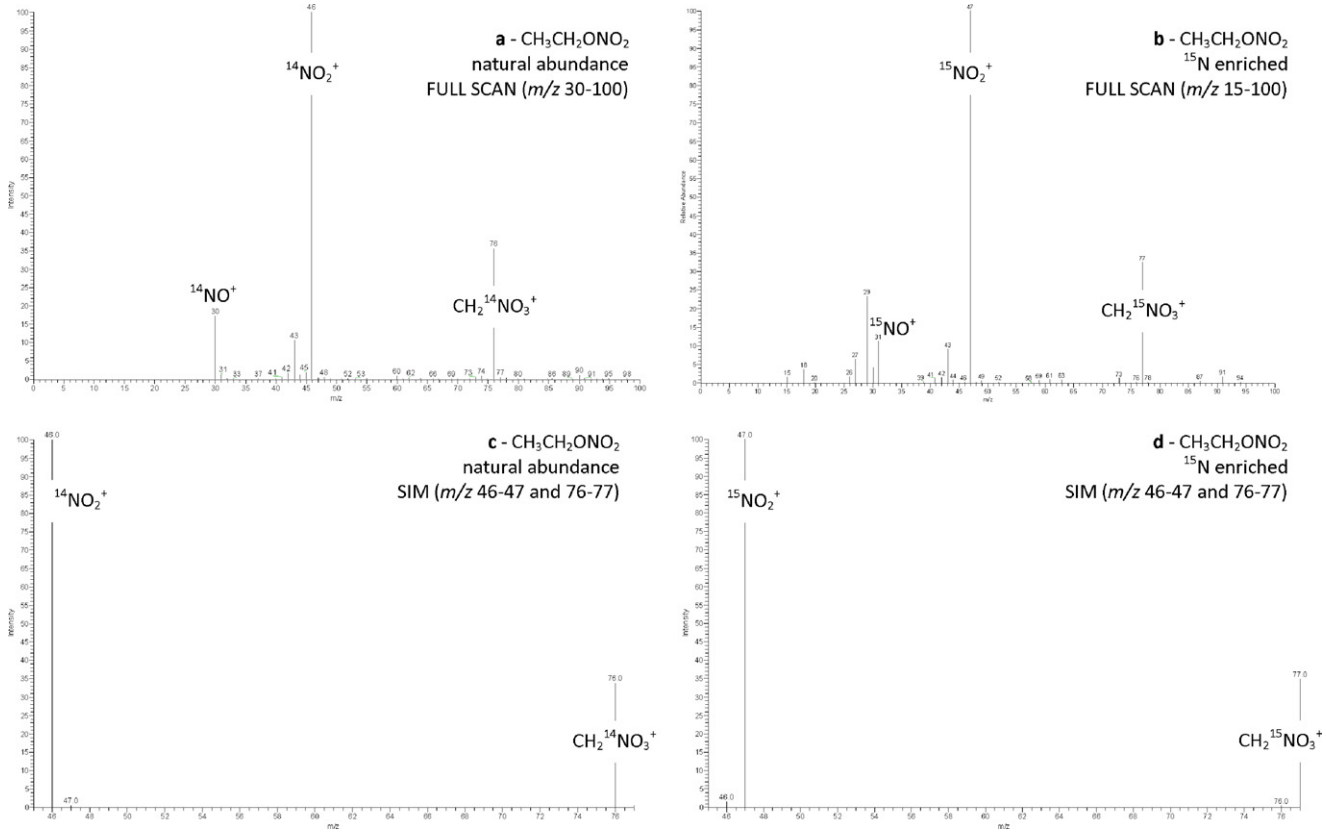

Fig. 2. Nitric acid ethyl ester, $CH_3CH_2ONO_2$. (a) Full scan mass spectra (m/z 30–100) of the standard of natural origin. (b) Full scan mass spectra (m/z 15–100) of the ^{15}N enriched standard. (c) SIM mass spectra (m/z 46–47 and 76–77) of the standard of natural origin. (d) SIM mass spectra (m/z 46–47 and 76–77) of the ^{15}N enriched standard.

use for classical isotope dilution methodology, but here some considerations have been given to correct for the problem of conversion of NO_2^- to NO_3^- and the instrumental mass bias which results in isotope ratios different from their values expected from the natural and enriched abundances of ^{14}N and ^{15}N.

Defining N_x and N_y as the signals (m/z 30 and 31) measured from 10 mg/l NO_2^- standard of natural origin and E_x and E_y as the signals (m/z 30 and 31) measured from 10 mg/l NO_2^- isotopically enriched species, it is possible to define the following parameters (^xA_N, ^xA_E, ^yA_N, ^yA_E):

$$\begin{cases} {}^xA_N = \dfrac{N_x}{N_x + N_y} \\ {}^xA_E = \dfrac{E_x}{E_x + E_y} \\ {}^yA_N = \dfrac{N_y}{N_x + N_y} \\ {}^yA_E = \dfrac{E_y}{E_x + E_y} \end{cases} \quad (1)$$

If the MS signals are not affected by mass bias, the above definitions of ^xA_N, ^xA_E, ^yA_N, ^yA_E will be simply the relative abundances of ^{14}N and ^{15}N in the natural and enriched samples.

Defining X_1 and Y_1 as the signals (m/z 30 and 31) measured from the blend of the sample spiked with isotopically enriched standard and N_1 and E_1 as the fraction of analyte from natural and enriched origin in this blend, we can write:

$$\begin{cases} X_1 = {}^xA_N \cdot N_1 + {}^xA_E \cdot E_1 \\ Y_1 = {}^yA_N \cdot N_1 + {}^yA_E \cdot E_1 \end{cases} \quad (2)$$

The concentration of the analyte C_A in the sample is related to the concentration of enriched standard C_E and is given by:

$$C_A = C_E \cdot \frac{N_1}{E_1} \quad (3)$$

An approximate value for C_A should be obtained based on the value of C_E calculated from the gravimetric preparation of the enriched standard. In any case, the best results are obtained by measuring the value of C_E using the same method in order to take into consideration the effects which arise from the conversion of nitrite and from mass bias. In other words, C_E becomes an empirical quantification parameter.

Its value can be calculated by reverse isotope dilution, for which a second blend prepared from a standard of nitrite with a known concentration C_A^0 close to that of the sample C_A, and spiked with the same amount of enriched standard is processed. If there are no significant matrix effects, the response of this second blend and of the sample must be similar. Additionally, the chemical behavior and interferences will also be similar.

Defining X_2 and Y_2 as the signals (m/z 30 and 31) measured from this standard spiked with isotopically enriched compounds and N_2 and E_2 as the fraction of analyte from natural and enriched origin present, it is possible to write:

$$\begin{cases} X_2 = {}^xA_N \cdot N_2 + {}^xA_E \cdot E_2 \\ Y_2 = {}^yA_N \cdot N_2 + {}^yA_E \cdot E_2 \end{cases} \quad (4)$$

The concentration of the standard C_A^0 is accurately known, so the concentration of enriched standard C_E is given by:

$$C_E = C_A^0 \cdot \frac{E_2}{N_2} \quad (5)$$

The final equation is obtained by substitution of C_E from (5) into (3):

Table 1
Summary of results for determination of nitrite and nitrate in MOOS-1.

Nitrite (μM)		Nitrate (μM)	
HS-GC–MS	SPME-GC–MS	HS-GC–MS	SPME-GC–MS
3.15	3.19	21.7	21.3
3.15	3.42	22.3	23.5
3.20	3.48	22.3	23.8
3.15	3.21	22.4	23.4
3.16 ± 0.03	**3.3 ± 0.2**	**22.2 ± 0.3**	**23 ± 1**

Certified values: nitrite 3.06 ± 0.15 μM; nitrite and nitrate: 23.7 ± 0.9 μM.
Bold line reports the mean of four independent measurements performed using HS and SPME. The results are coherent and provide evidence that the precision achieved with the HS method is better than that with SPME. The overall mean between these data is given by: nitrite 3.2 ± 0.1 μM; nitrate 22.6 ± 0.9 μM; nitrite and nitrate: 26 ± 1 μM.

$$C_A = C_E \cdot \frac{N_1}{E_1} = C_A^0 \cdot \frac{E_2}{N_2} \cdot \frac{N_1}{E_1} = C_A^0 \cdot \frac{{}^yA_N \cdot X_2 - {}^xA_N \cdot Y_2}{{}^yA_N \cdot X_1 - {}^xA_N \cdot Y_1} \cdot \frac{{}^yA_E \cdot X_1 - {}^xA_E \cdot Y_1}{{}^yA_E \cdot X_2 - {}^yA_E \cdot Y_2} \quad (6)$$

Defining:

$$\begin{cases} \theta_N = \dfrac{{}^xA_N}{{}^yA_N} \\ \theta_E = \dfrac{{}^xA_E}{{}^yA_E} \end{cases} \quad (7)$$

the formalism of (6) becomes:

$$C_A = C_A^0 \cdot \frac{X_2 - \theta_N \cdot Y_2}{X_1 - \theta_N \cdot Y_1} \cdot \frac{X_1 - \theta_E \cdot Y_1}{X_2 - \theta_E \cdot Y_2} \quad (8)$$

The above discussion is focused on nitrite, but the same is valid for nitrate (m/z 46 and 47). Equation (8) presents the final formula used for the calculation. This is not a conventional way of employing an isotopically enriched standard for quantification purposes; indeed, equation (8) does not depend on the concentration of enriched standard or on the relative abundances of $^{14}N/^{15}N$ in the sample and in the internal standard. From this point of view, this procedure is quite different from a rigorous isotope dilution methodology. Here, calibration is achieved through the values of θ_N, θ_E and X_2, Y_2, which are empirical parameters obtained from measurements performed in a particular instrumental setting characteristic of the experiments. In all measurements, a solution containing 2.17 μM NO_2^- and 16.1 μM NO_3^- was used in the reverse experiment for calibration purposes (X_2, Y_2 value).

3.3. Quantification of nitrite and nitrate in MOOS-1

Quantitative data related to analytical content of nitrite and nitrate in MOOS-1 (Seawater Certified Reference Material for Nutrients) are summarized in Table 1. The related chromatogram is presented in Fig. 3. In order to perform quantification, ion extraction at m/z 30–31 and at m/z 46–47 was carried out for nitrite and nitrate respectively; peak heights were employed for all calculations. All data reported are obtained applying equation (8). Other experiments not reported here, based on the classical internal standard (IS) and on standard additions (SA), provided results in accord with those summarized in Table 1. Furthermore, the slopes of both SA and IS plots were consistent, suggesting that matrix effects were accounted for by the use of the enriched standard.

Regarding analytical figures of merit, instrumental detection limits (concentration of the analyte that produces a peak with a signal-to-noise ratio of 3) with HS-GC–MS are 0.07 μM for NO_2^- and 2 μM for NO_3^- and with SPME are 0.3 μM for NO_2^- and 2 μM for NO_3^-. Analytical performance can be improved by increasing

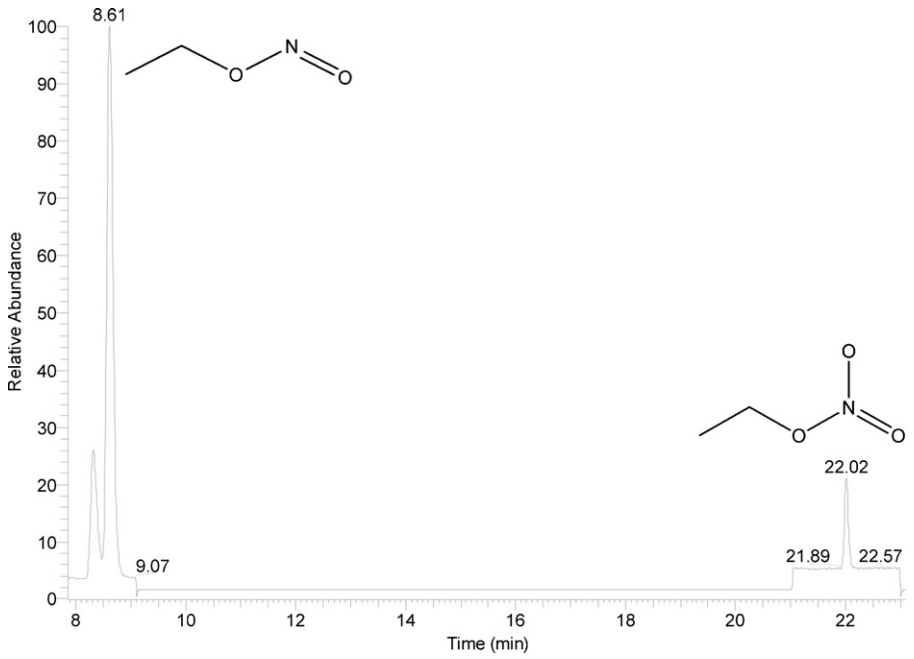

Fig. 3. HS-GC–MS chromatogram collected in SIM mode during analysis of MOOS-1 sample. Nitrite ion: converted into ethyl ester nitrous acid, retention time 8.61 min, mass extracted 30. Nitrate ion: converted into ethyl ester nitric acid, retention time 22.02 min, mass extracted 46. The peak eluting in front of ethyl nitrite is methoxyethane, an impurity arising from the triethyloxonium tetrafluoroborate.

Table 2
Recovery test performed on MOOS-1.

Nitrite (μM)				Nitrate (μM)			
Added	Expected	Found	Rec. (%)	Added	Expected	Found	Rec. (%)
0	3.06	3.21	105.0	0	20.6	22.2	107.6
0	3.06	3.17	103.5	0	20.6	22.4	108.5
2.72	5.78	5.77	99.8	20.2	40.8	44.8	109.8
2.72	5.78	5.75	99.6	20.2	40.8	43.2	105.7
5.43	8.49	8.09	95.2	40.4	61.0	62.9	103.1
5.43	8.49	8.10	95.3	40.4	61.0	62.1	101.7
10.87	13.93	12.91	92.7	80.8	101.4	106.5	105.1
10.87	13.93	13.27	95.3	80.8	101.4	106.3	104.8

The recovery (Rec., %) has been calculated as the ratio of measured response (found) and concentration expected (expected). A bias of less than 10% is evident.

Table 3
Recovery test performed on mineral water.

Nitrite (μM)			Nitrate (μM)
Added	Found	Rec. (%)	Found
0	n.d.	–	121.3
0.22	0.20	92.3	117.5
2.15	2.15	99.8	120.7
21.52	21.06	97.9	116.8
215.21	203.95	94.8	107.7

Calibration in based in all cases on reverse calibration performed with a solution of 2.17 μM NO_2^- and 16.1 μM NO_3^-.

the temperature of the HS, the amount of HS injected and time of exposure of the SPME fiber to the HS.

From Table 1, it is evident that there are no significant differences between the concentrations of nitrite and nitrate obtained using HS-GC–MS and SPME-GC–MS procedures. The overall mean of the results for the concentration of nitrite is 3.2 ± 0.1 μM (RSD 4.0%, $n = 8$) and for the concentration of nitrate is 22.6 ± 0.9 μM (RSD 4.0%, $n = 8$). The sum of nitrite and nitrate can be calculated to be 26 ± 1 μM (RSD 4.0%, $n = 8$). These results are in excellent agreement with the certified values for MOOS-1, i.e. 3.06 ± 0.15 μM for nitrite and 23.7 ± 0.9 μM for nitrite and nitrate.

Table 2 reports results for a recovery test performed on MOOS-1; the values obtained confirm not only the accuracy of this analytical method but that it is able to correct for the conversion of nitrite to nitrate. Finally, Table 3 presents recovery data for nitrite from a mineral water containing no detectable concentration of nitrite. Four additions at different concentrations of nitrite were performed spanning more than three orders of magnitude of concentration. Despite calculation of X_2 and Y_2 from equation (8) being based in all cases on the reverse experiment performed on a solution of 2.17 μM NO_2^- and 16.1 μM NO_3^-, no errors are evident for the recovery of nitrite and quantification of nitrate was satisfactory: 117 ± 5 μM (RSD 4.7%, $n = 5$) against 105 μM as the expected value. All instrumental and chemical problems possibly arising with this procedure are well corrected for by the use of the enriched standard and by the selected method of quantification, which demonstrates the ruggedness that the use of an enriched standard imparts to an analytical procedure.

4. Conclusion

Aqueous phase alkylation with TEOT has been applied to the determination of nitrite and nitrate in a sample of seawater certified reference material (MOOS-1) by CVG-GCMS. Nitrite and nitrate were converted to their corresponding volatile ethyl esters and could be simultaneously detected and determined using different approaches, including HS-GC–MS and SPME-GC–MS. The two procedures provide similar analytical figures of merit and direct HS is preferred for analysis when manual injection is performed, while SPME should be selected when the automation of the procedure is required. The results obtained for MOOS-1 using an isotopically enriched internal standard for quantification provided results in excellent agreement internally and with the certified values. The problem of chemical inter-conversion of nitrite to nitrate (less than 10%) is well accounted for using the present method. To the best of our knowledge, this is the first CVG method developed for the simultaneous determination of nitrite and nitrate: CVG offers the advantages of good analytical

figures of merit while separating the derivatized analytes from the sample matrix. Moreover, use of enriched isotopes makes available the ultimate primary calibration technique of isotope dilution. A reverse spike against a primary natural abundance standard affords traceability, making the method suitable for certification purposes and promising for application to samples of different origin.

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