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Journal of Chromatography A, 848 (1999) 327–335

JOURNAL OF CHROMATOGRAPHY A

Evaluation of dynamic headspace and purge-and-trap techniques for the high-resolution gas chromatography analysis of nitrous oxide in seawater

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Received 24 December 1998; received in revised form 17 March 1999; accepted 23 March 1999

Abstract

The present study focuses on the effectiveness of dynamic headspace (DH) and purge-and-trap (PT), which are two commonly used techniques for determining volatile organic compounds in environmental samples, on the extraction and trace analysis of nitrous oxide in seawater. With the aim of obtaining reliable quantitative data in the DH and in the PT techniques, kinetics of these processes were studied; a first-order kinetic-like function is found to be followed for the extraction of nitrous oxide in both the DH and PT sampling methods. A three-way analysis of variance was carried out to evaluate the effect of the water sample composition on DH and PT analysis in order to systematically and accurately examine the effect of different factors on the chromatographic response of N_2O; a significant matrix effect proportional to the nitrous oxide concentration was observed when bidistilled water, synthetic and natural seawater were considered. The effects of different sampling procedures were evaluated in terms of linearity range, limit of detection, capability of detection, precision, extraction recovery and accuracy. Better results in terms of extraction recovery, sensitivity and detection limit were obtained when applying the purge-and-trap technique combined with GC–electron-capture detection; detection limits at very low pmol ml^{-1} levels were achieved, making this procedure suitable for trace nitrous oxide analysis in marine samples.
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Keywords: Headspace analysis; Water analysis; Environmental analysis; Purge-and-trap methods; Sample handling; Nitroux; Nitrous oxide

1. Introduction

Atmospheric nitrous oxide (N_2O) plays a primary role in global processes [1] and has the potential to contribute about 300 times to the greenhouse effect relative to carbon dioxide; it also affects the ozonosphere. Therefore the current increase in the atmospheric N_2O is assumed to have the potential to impact global climate over the next century. Its atmospheric concentration of around 310 ppb is increasing at the rate of about 0.3% per year [2]. Biomass burning and microbial processes such as nitrification and denitrification are the principal sources of atmospheric N_2O [3].

Intensive efforts to characterise marine N_2O fluxes

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PII: S0021-9673(99)00423-9

were made starting from the 1960s. This activity was prompted by the general interest in identifying significant sources of N_2O due to the hypothesised role of N_2O in stratospheric ozone depletion [4]. Nitrous oxide is a trace constituent in seawater, generally present at concentration in the $1–10 \cdot 10^{-9}$ mol l^{-1} range; it is often found at levels in excess with respect to that required for the atmospheric equilibrium: a slight supersaturation of N_2O is present in most oceanic waters and concentrations often increase with depth, reaching maxima at mid-depths. These observations indicate that the oceans are probably a net source of N_2O to the atmosphere [5]. Even though abiotic reactions may yield N_2O, in the sea a biotic source is usually assumed [5]. Nitrous oxide is an intermediate, and a potential end product, of biological denitrification; N_2O can either be consumed or evolved during denitrification. Two decades ago, denitrification was generally considered the primary source of N_2O. However, biological nitrification can also produce N_2O, either as a result of the breakdown of an unstable enzyme bound intermediate during ammonium oxidation, or through a reductive, detoxification pathway during nitrite accumulation.

The need to determine nitrous oxide accurately in water and in sediment samples for environmental monitoring is growing. Various techniques have been used for the analysis of nitrous oxide in biological and environmental samples, gas chromatographic methods being the most frequently applied [6–14]. Separation of N_2O from other gases have been performed on GC columns packed with Porapak [6,8–12,14] or molecular sieve [6–8]; recently, a gas chromatographic method based on the use of a fused-silica column coated with a porous layer of Porapak Q has been reported for the determination of nitrous oxide in the presence of phosphine [13]. These separation techniques usually employ thermal-conductivity or electron-capture detectors [6–10,12,14]; mass spectrometry has been successfully proposed for the mass selective detection of nitrous oxide in biological matrices [11], whereas flame-photometric detection has proven useful for the determination of N_2O in the presence of phosphine [13].

Stable isotope studies are recognized to be diagnostic for obtaining information about transformation mechanism on trace species. Measurements of stable isotope $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios of atmospheric nitrous oxide have been reported [3,15,16]. In a recent report, high-precision mass spectrometric isotopic determination of both the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios in N_2O has been proposed [17].

Concerning sampling techniques, static headspace analysis is the most common one for nitrous oxide in environmental and biological samples [7,11,12]. A limitation of this headspace method is that extraction is not exhaustive and since it relies on equilibrium partitioning of the analytes between the sample matrix and a gas phase, it is solely determined by the gas/sample matrix partition coefficient and therefore by the interactions of N_2O with the matrix. Hence, the technique is not suitable for the determination of trace analytes and a strong matrix dependence of the response is observed.

At present, other extractive sampling techniques, such as dynamic headspace and purge-and-trap, for subsequent determination by GC have been not explored in the case of nitrous oxide. Both these procedures involve analyte trapping and concentration by cryofocusing at the head of the chromatographic system, thus allowing trace enrichment depending on the sampling time.

The present study focuses on the effectiveness of dynamic headspace (DH) and purge-and-trap (PT), which are two commonly used techniques for determining volatile organic compounds in environmental samples, on the extraction and trace analysis of nitrous oxide in seawater.

Using electron-capture detection (ECD), the results were evaluated in terms of sensitivity, linearity range, limit of detection, capability of detection, precision, accuracy and extraction recovery for both techniques. With the aim of obtaining reliable quantitative data in the DH and in the PT processes without the use of internal standards, kinetics of these processes were studied by calculating the stripping/purging rate constant.

2. Experimental

2.1. Apparatus

The sampling apparatus used for headspace and

purge-and-trap experiments was the TCT/PTI Chrompack CP4010 (Chrompack, Middelburg, The Netherlands).

Dynamic headspace experiments were carried out using a standard Pyrex vessel with a 3-port sample chamber (Chrompack). A standard fritted-glass purging vessel was used for purge-and-trap analysis; the volume of the sample chamber was 30 ml and the injection port of the vessel was modified to introduce the gaseous analyte directly in the purge flow. Helium was used as the stripping/purging gas.

Before each analysis, a blank measurement using an empty vessel flushed with helium was performed.

For the DH and the PT techniques, the conditions used were as follow: sample temperature, 20°C; stripping time (DH) or purge time (PT), 10 min; stripping (DH) or purge (PT) flow gas, 8 ml min^{-1} helium; cooler water trap temperature, −10°C; cryogenic trap, RT-Q Plot (divinylbenzene) capillary (30 cm×0.53 mm I.D., d_f=20 μm) (Restek, Bellefonte, PA, USA); cryogenic trap temperature, −150°C; desorb temperature, 175°C; desorb time, 1 min (heating rate 5°C s^{-1}). Since aqueous matrices were used, a water trap was necessary: in fact, the swept water must be selectively condensed before reaching the cryogenic trap, which would otherwise be blocked.

Both the purge-and-trap and headspace sample introduction systems were connected to a Hewlett-Packard Model 5890 gas chromatograph (Palo Alto, CA, USA) equipped with an electron capture detector operating at 300°C. The detector signals were monitored using the Turbochrom 4 PE Nelson data acquisition system (PE Nelson, Cupertino, CA, USA). Chromatographic separation was achieved on a RT-Q Plot wide-bore column (25 m×0.53 mm I.D., d_f=20 μm) (Restek). The column temperature was held at 30°C for 5 min, then increased from 30 to 150°C at 20°C min^{-1}, holding this temperature for 2 min. Helium at a flow rate of 5 ml min^{-1} was used as carrier gas.

2.2. Statistical analysis

Calculations were performed with the Statgraphics statistical package (Manugistics, Rockville, MD, USA).

2.3. Chemicals

A gaseous standard of nitrous oxide in nitrogen at a concentration of 1000 ppm (v/v) was purchased from Rivoira (Florence, Italy). This standard was contained in a gas cylinder equipped of a pressure-reducer and a pressure regulator. Aliquots of the gaseous standard were withdrawn as needed using a 2.5-ml gas-tight syringe; the working standards were prepared daily from the 1000 ppm-gaseous standard.

Laboratory bidistilled water was used as a reference aqueous matrix. All other chemicals (sodium chloride, magnesium sulphate, sodium hydrogen carbonate) were of analytical-reagent grade and were supplied by Carlo Erba (Milan, Italy).

Synthetic seawater was prepared by adding to bidistilled water a sea-salt mixture to simulate natural seawater: approximately 30 g sodium chloride, 10 g magnesium sulphate and 0.05 g sodium hydrogen carbonate were added to 1 l bidistilled water.

3. Results and discussion

The chromatogram of the GC–ECD analysis of nitrous oxide in a spiked seawater sample ($1.93 \cdot 10^{-9}$ mol ml^{-1}) is given in Fig. 1 together with a blank made up of the unspiked sample. The use of a capillary wide-bore column, the efficient solute focusing step in the cryogenic trap and the fast heating rate in the injection step allowed us to obtain high efficiency, with number of theoretical plates of about 30 000 for the N_2O peak. These results were obtained using the DH technique, but PT behaves similarly from the point of view of the chromatographic results.

3.1. Dynamic headspace and purge-and-trap techniques

In a first step, the stripping (DH) and purging (PT) rates in the corresponding extraction processes were calculated for bidistilled water.

Both the sampling techniques were then checked for their performance as regards the following characteristics: calibration function, detection limit, capability of detection, precision, accuracy and extraction recovery.

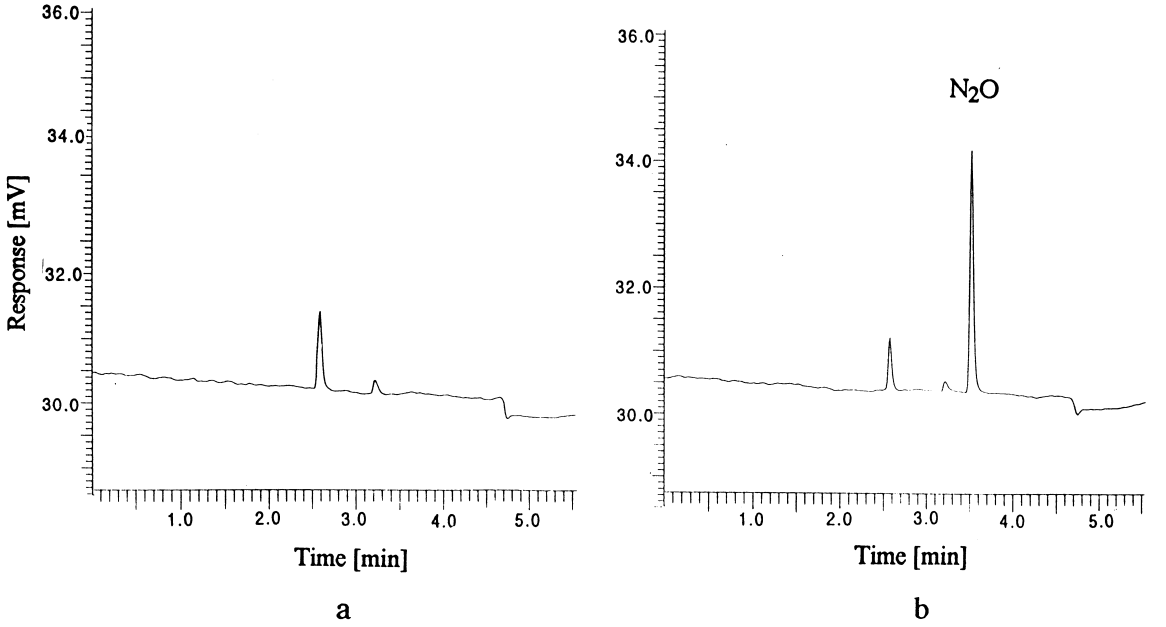

Fig. 1. Dynamic headspace GC–ECD analysis of (a) unspiked seawater and (b) seawater spiked with N_2O at a concentration of $1.93 \cdot 10^{-9}$ mol ml^{-1}. For sampling and chromatographic conditions see Experimental.

3.1.1. Kinetics of the dynamic headspace and purge-and-trap techniques

With the aim of obtaining reliable quantitative data with the DH and the PT techniques, kinetics of these processes were studied. The recovery in the DH technique should be controlled by the diffusion rate of N_2O from the liquid to the gaseous phase of the sample [18]. An infinitesimal variation in concentration of the liquid phase, dc_1 can be described by the equation:

$$dc_1 = (JA/V)\,dt \quad (1)$$

where J is the flux of N_2O from the solution to the gas phase (mol cm^{-2} s^{-1}), A is the interphase area (cm^2) and V is the volume of the solution (ml). In accordance with the first Fick's law and with the Nernst approximation, Eq. (1) can be rewritten:

$$dc_1/c = -(D/h\delta)\,dt \quad (2)$$

where D is the N_2O diffusion constant, δ is the thickness of the diffusion layer, and h is the height of the liquid phase in the vessel.

Under the boundary conditions that $c_1 = c_0$ when $t = 0$, integration leads to a first order kinetic-like function:

$$c_1 = c_0 \exp(-bt) \quad (3)$$

b being equal to $D/(h \cdot \delta)$

Eq. (3) was tested by performing five subsequent DH experiments, each for a period of 3 min, on a bidistilled water sample containing $6.93 \cdot 10^{-9}$ mol ml^{-1} of nitrous oxide. The analyte concentration in the liquid phase was determined after each extraction step (Table 1). Results are plotted in Fig. 2.

In the case of the headspace technique, the equation calculated by non-linear least squares method is:

$$c_1 = 6.87(\pm 0.13) \exp[-0.177(\pm 0.006)]t$$

Analogously, for the purge-and-trap sampling, the value of b can be determined from the calibration curve:

$$c_1 = 7.03(\pm 0.26) \exp[-0.266(\pm 0.020)]t$$

The higher value of b found for the purge-and-trap sampling, can be explained taking into account the larger interphase area, which is due to the presence of inert gas bubbles inside the solution. In the case of the PT technique, the term A/V is higher than $1/h$. Moreover, owing to convection induced by bubbling

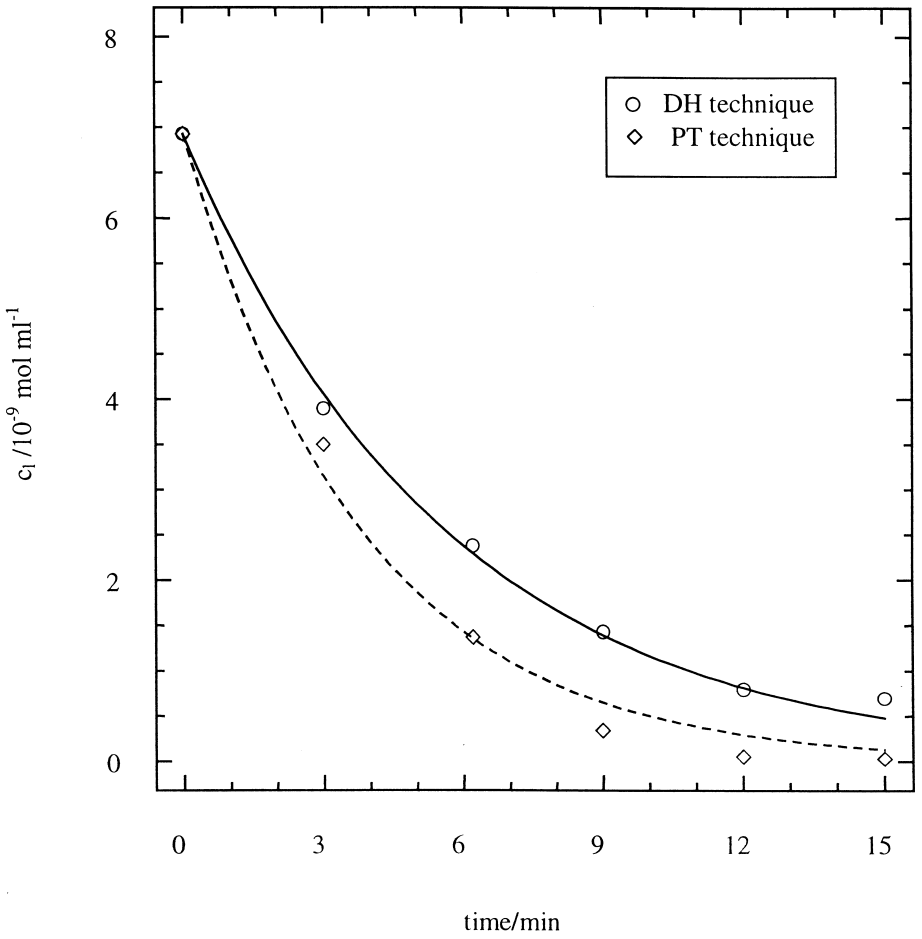

Fig. 2. Variation of N_2O concentration in the liquid phase vs. time using the DH and PT techniques.

of purging gas in the solution, the diffusion layer should be thinner in PT than in DH technique.

The half-time of the stripping process, $t_{1/2}$, is obtained by solving the equation:

$$c_1/c^\circ_1 = 0.5 = \exp(-bt_{1/2}) \quad (4)$$

from which values of 3.9 (±0.1) and 2.6 (±0.2) min were calculated for DH and PT respectively. Similarly, the time necessary to reach the completion of extraction process, $t_{99.9}$, resulted to be 39 (±1) min (DH technique) and 26 (±2) min (PT technique) and could be calculated from:

$$c_1/c^\circ_1 = 0.001 = \exp(-bt_{99.9}) \quad (5)$$

Then, using the kinetic equation the calculated extraction recoveries in the experimental conditions chosen (stripping/purging time = 10 min; $c^\circ_1 = 6.93 \cdot 10^{-9}$ mol ml^{-1}) were 83.4 (±0.6)% for DH and 93.0 (±0.3)% for PT.

3.1.2. Study of the effects of water sample composition on the GC response of nitrous oxide

In order to systematically and accurately examine the effect of different factors on the chromatographic response of N_2O, the analysis of variance (ANOVA) was carried out. First, a three-way ANOVA with interactions was performed on the GC responses of nitrous oxide. The three classification factors were as follows: (a) concentrations of N_2O in the aqueous samples; (b) nature of the aqueous sample; (c) analytical technique. As measurements were carried

Table 1
Change of the nitrous oxide concentration in the liquid phase (bidistilled water) in the time, as determined in subsequent extraction steps of the gaseous component by the DH and PT techniques[a]

Time/min	DH technique $c_1/1\cdot10^{-9}$ mol ml^{-1}	PT technique $c_1/1\cdot10^{-9}$ mol ml^{-1}
3	3.90±0.06	3.50±0.06
6	2.38±0.09	1.37±0.02
9	1.43±0.16	0.34±0.02
12	0.80±0.14	0.056±0.006
15	0.70±0.09	0.034±0.002

[a] Average of three individual determinations.

out in triplicate, a set of 126 determinations was performed for this purpose. This analysis showed a slightly significant ($p=0.03$) third order interaction, so that no general inference could be made. Therefore the 126 data were split into two sets of 63 data, the first for the DH method and the second for PT; two two-way ANOVA were carried out, resulting in both cases in highly significant ($p<0.01$) differences for the main effects (concentrations and matrices) as well as for interactions. For both the techniques, the highest GC response of N_2O was obtained in synthetic seawater and the lowest in natural seawater; the composition of these samples is responsible for the different concentration of the volatile compound in the gaseous phase. In fact, two opposite effects occur in the analyte extraction from seawater: the presence of high salt concentrations determines an increase of the concentration of the volatile compound in the gaseous phase ('salting-out' effect) [19], whereas the presence of organic substances or suspended material can reduce the partition of N_2O towards the gas phase [20]. This difference increased with increasing concentration of nitrous oxide for seawater and synthetic seawater (second order interaction); thus, a significant matrix effect proportional to the concentration is observed. The significance of the third order interaction accounts for the higher increase of differences in the response with nitrous oxide concentration between distilled water and seawater for the PT technique than for HD.

3.1.3. Calibration graph, detection limit, capability of detection and precision

Using the DH technique, quantification was carried out by the external standard method; up to seven levels of N_2O standard were prepared in the 0.28–$6.93\cdot10^{-9}$ mol ml^{-1} (12.32–$305\cdot10^{-9}$ g ml^{-1}) range. The peak area responses resulting from the mean of three replicate analyses of each standard were used to define the best-fit regression equation and the data were modelled by least-squares linear regression. The figures of merit of these calibration graphs are quoted in Table 2.

Applying the PT method, a linear relationship in the same concentration range was found for the aqueous samples examined (Table 3). As it was shown by ANOVA, the PT technique appears to be more sensitive than DH, as was shown by the significantly higher slopes of the calibration graph; regards the water samples, both the methods demonstrate the highest sensitivity for the assay of nitrous oxide in synthetic seawater.

The detection limit was calculated for N_2O in each water sample in the traditional way as the concentration of analyte which increases the signal of the blank by three times its standard deviation. Detection limits at the pmol ml^{-1} level were achieved for this analyte using the DH technique in all aqueous samples considered (Table 4). These

Table 2
Analytical figures of merit for the analysis of nitrous oxide in different aqueous samples by the dynamic headspace technique[a]

Sample type	Calibration equation[b]	r^2	S_{xo}[c] (10^{-9} mol ml^{-1})	V_{xo}[d] (%)
Bidistilled water	$y=103\ (\pm13)\cdot10^3+150\ (\pm3)\cdot10^3x$	0.996	0.19	5.9
Seawater	$y=78\ (\pm15)\cdot10^3+131\ (\pm4)\cdot10^3x$	0.995	0.25	7.8
Synthetic seawater	$y=113\ (\pm18)\cdot10^3+157\ (\pm4)\cdot10^3x$	0.995	0.25	7.8

[a] Linear range: 0.28–$6.93\cdot10^{-9}$ mol ml^{-1} ($n=21$).
[b] y=GC peak area of nitrous oxide in μV s; x=concentration of nitrous oxide in 10^{-9} mol ml^{-1}.
[c] Standard deviation of the method.
[d] Relative standard deviation of the method.

Table 3
Analytical figures of merit for the analysis of nitrous oxide in different aqueous matrices by purge-and-trap technique[a]

Sample type	Calibration equation[b]	r^2	S_{xo}[c] (10^{-9} mol ml^{-1})	V_{xo}[d] (%)
Bidistilled water	$y=120\ (\pm 9)\cdot 10^3+158\ (\pm 2)\cdot 10^3 x$	0.998	0.14	4.4
Seawater	$y=71.3\ (\pm 1.6)\cdot 10^3+141\ (\pm 6)\cdot 10^3 x$	0.995	0.36	11.2
Synthetic seawater	$y=120\ (\pm 1.4)\cdot 10^3+179\ (\pm 4)\cdot 10^3 x$	0.996	0.21	6.6

[a] Linear range: $0.28–6.93\cdot 10^{-9}$ mol ml^{-1} ($n=21$).
[b] y = GC peak area of nitrous oxide in μV s; x = concentration of nitrous oxide in 10^{-9} mol ml^{-1}.
[c] Standard deviation of the method.
[d] Relative standard deviation of the method.

DLs are lower than those previously reported by other authors for nitrous oxide, obtained using the static headspace method and MS and flame-photometric detection [10,12]. In the case of the PT technique, the limit of detection of the analyte in bidistilled water resulted to be four times lower than that obtained using the DH technique (Table 4). A similar ratio between the detection limit values of nitrous oxide obtained using the PT and the DH techniques in seawater and synthetic seawater was observed.

Taking into account that nitrous oxide is a trace constituent in environmental samples, a further different approach was applied to significantly distinguish the signal of the analyte from that of a blank and to obtain a quantitative result with adequate precision; for this purpose, using the calibration function the capability of detection (XN) was determined [21,22]. The results are given in Table 4 for both the techniques. Similarly to that observed in the case of detection limits, the minimum XN value was obtained for synthetic seawater ($30.1\cdot 10^{-12}$ mol ml^{-1} for DH and $11.1\cdot 10^{-12}$ mol ml^{-1} for PT), whereas the matrix effect in seawater resulted to also affect capability of detection ($46.2\cdot 10^{-12}$ mol ml^{-1} for DH and $28.7\cdot 10^{-12}$ mol ml^{-1} for PT).

The precision was established by repeating five analyses on 0.28 and $6.93\cdot 10^{-9}$ mol ml^{-1}. When applying the DH technique, the RSDs did not exceed 4.5% for all the aqueous samples tested; also the precision obtained for purge-and-trap replicate analyses was adequate and comparable to that for dynamic headspace.

3.1.4. Accuracy of the sampling methods for the determination of nitrous oxide in seawater

Since ANOVA evidenced a matrix effect for both the DH and PT techniques, it was determined a

Table 4
Determination of the detection limit (DL) and of capability of detection (XN) using the calibration function for the analysis of nitrous oxide in different aqueous samples by the DH and PT techniques[a]

Aqueous sample	Calibration equation[a]	r^2	Linear range[b] / $1\cdot 10^{-12}$ mol ml^{-1}	DL[c] (10^{-12} mol ml^{-1})	XN
(a) DH technique					
Bidistilled water	$y=3.94(\pm 0.17)\cdot 10^5 x$	0.995	41.6–280.0	1.28	33.7
Seawater	$y=3.21\ (\pm 0.19)\cdot 10^5 x$	0.996	53.2–280.0	3.19	46.2
Synthetic seawater	$y=4.27\ (\pm 0.13)\cdot 10^5 x$	0.996	35.4–280.0	0.64	30.1
(b) PT technique					
Bidistilled water	$y=4.68\ (\pm 0.17)\cdot 10^5 x$	0.997	30.3–280.0	0.32	20.9
Seawater	$y=4.20\ (\pm 0.14)\cdot 10^5 x$	0.992	35.4–280.0	0.64	28.7
Synthetic seawater	$y=4.92\ (\pm 0.11)\cdot 10^5 x$	0.996	14.6–280.0	0.20	11.1

[a] y = GC peak area of nitrous oxide in μV s; x = concentration of nitrous oxide in 10^{-12} mol ml^{-1}.
[b] $n=21$.
[c] Detection limit calculated as 3σ/slope of the calibration curve.

recovery function (Eq. 6) [21], in order to establish if constant as well as proportional systematic deviations were present in the determination of N_2O in seawater. For this purpose, a blank synthetic matrix could not be used, since analysis of variance provided evidence of a significative difference between the extractable fraction of N_2O from natural and from synthetic seawater. Therefore, the recovery function was calculated by spiking natural seawater samples, in which the absence of nitrous oxide had been previously verified, to obtain seven nitrous oxide concentrations in the $0.28–6.93 \cdot 10^{-9}$ mol ml^{-1} range like those in the model reference solution used in the calibration. These samples were then submitted to the entire DH or PT and GC analysis. No significant differences resulted from the comparison of the variances ($p=0.4$) of the function referred to seawater sample (s^2_{sw}) and that of the fundamental analytical procedure (s^2_{fc}), so allowing the calculation of the recovery function. For this purpose, the coefficients of the calibration function of the fundamental analytical procedure (Tables 2 and 3) were used to calculate the found concentrations x_f from the signal values y_f found for seawater. The recovery function was then obtained:

$$x_f = a_f + b_f x_c \quad (6)$$

where x_c are the concentration of N_2O in the spiked sample.

The regression parameters for the recovery curve are summarised in Table 5 for the two techniques. Slopes and intercepts of both the recovery functions did not significantly differ from 1 and 0 respectively. A new recovery function having $a_f=0$ was then calculated for each method; significant proportional systematic errors were detected, since the calculated slope resulted to be significantly different from 1. It can be then inferred that for an accurate quantitation of nitrous oxide in seawater, the method of standard addition is recommended both for the DH and PT techniques.

In addition, the recovery rate (RR) could be calculated as RR (%)$=100\ b_f$. This value resulted to be 84.4% for DH and 94.0% for PT. Therefore, as expected by using the purge-and-trap technique, better recoveries of N_2O from seawater than those obtained by the dynamic headspace method were achieved; these recoveries are associated with the ability of the purging gas to trap the gaseous analyte from solutions. Recovery of the analyte was over 90% in the range of nitrous oxide concentrations explored, when seawater was considered.

Table 5
Regression parameters for the recovery function for the dynamic headspace and purge-and-trap techniques[a]

(a) DH technique			
Regression equation: $x_f = a_f + b_f x_c$			
Equation[b]	r^2	t_{a_f}	P[c]
$x_f = -2.2\ (\pm 1.5) + 0.87\ (\pm\ 0.03)\ x_c$	0.997	1.48	0.20
Regression equation: $x_f = b_f x_c$			
Equation[b]	r^2	t_{b_f}	P[c]
$x_f = 0.844\ (\pm\ 0.016)\ x_c$	0.997	9.75	<0.01
(b) PT technique			
Regression equation: $x_f = a_f + b_f x_c$			
Equation[b]	r^2	t_{a_f}	P[c]
$x_f = -2.1\ (\pm 2.0) + 0.97\ (\pm\ 0.04)\ x_c$	0.99	1.05	0.34
Regression equation: $x_f = b_f x_c$			
Equation[b]	r^2	t_{b_f}	P[c]
$x_f = 0.94\ (\pm\ 0.02)\ x_c$	0.991	2.74	0.04

[a] Range: $0.28–6.93 \cdot 10^{-9}$ mol ml^{-1} ($n=21$).
[b] For the meaning of x_f and x_c see text.
[c] df$=5$, double-sided

4. Conclusions

Dynamic headspace was compared with purge-and-trap for the analysis of nitrous oxide in seawater. Better results in terms of extraction recovery, sensitivity and detection limit were achieved when applying purge-and-trap combined with GC–ECD. Detection limits at very low pmol ml^{-1} levels were obtained, making the methodology based on the use of PT–GC–ECD suitable for trace nitrous oxide analysis in marine samples.

Acknowledgements

The authors acknowledge financial support from the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (Italy) and from the European Commission's Marine Science and Technology Programme ''Preserving the Ecosystem'' under the

project NICE: Nitrogen Cycling in Estuaries (contract MAS3-CT96-0048). This paper is the ELOISE contribution no. 087.

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