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Determination of acetone in seawater using derivatization solid-phase microextraction

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Abstract

Acetone plays an important role in the chemistry of both the atmosphere and the ocean, due to its potential effect on the tropospheric HO_x (= HO + HO_2) budget, as well as its environmental and health effects. We discuss the development of a mobile, sensitive, selective, economical and facile method for the determination of acetone in seawater. The method consists of derivatizing acetone to its pentafluorobenzyl oxime using 1,2,3,4,5-pentafluorobenzylhydroxylamine (PFBHA), followed by solid-phase microextraction (SPME) and analysis by gas chromatography/mass spectrometry (GC/MS). A detection limit of 3.0 nM was achieved. The buffering capacity of seawater imposes challenges in using the method's optimum pH (3.7) on seawater samples, requiring calibration standards to be made in buffered salt water and the acidification of seawater samples and standards prior to extraction. We employed the technique for analysis of selected surface seawater samples taken on the Nordic seas during the ARK-XX/1 cruise (R.V. *Polarstern*). An upper limit of 5.5– 9.6 nM was observed for acetone in these waters, the first acetone measurements reported for far North Atlantic and Arctic waters.

Introduction

Acetone in the atmosphere is produced by the oxidation of propane and other larger molecular weight hydrocarbons or through direct emission by various species of plants [1, 2]. It may also be transferred to the atmosphere from surface seawater [3], where it is thought to be derived from the photodegradation of dissolved organic matter (DOM) [4, 5]; it has also been suggested to be produced directly by certain algae [6] and bacteria [7]. It can be readily exchanged between natural waters and air due to its low molecular weight and volatility. Interest in acetone, along with many other low molecular weight (LMW) carbonyl compounds, has increased due to their potential adverse health effects in drinking water [8]. Moreover, acetone can potentially alter the oxidizing potential of the troposphere through the production of HO_2 [1, 9]. One of the main sources of hydroxyl (OH) radicals in the troposphere is the reaction of water vapour with O (^{1}D) (Reactions 1 and 2).

$$O_3 + h\nu(\lambda \leq 320nm) \rightarrow O_2 + O^{\cdot}(^1D) \quad (1)$$

$$O^{\cdot}(^1D) + H_2O \rightarrow 2^{\cdot}OH \quad (2)$$

Since the upper troposphere is much dryer than the lower troposphere, the above pathway for the production of hydroxyl radicals is less efficient [10]. In this region of the troposphere, acetone contributes to the production of HO_x [10]. Indeed, by considering acetone photochemistry (photolysis and OH-initiated reactions) in HO_x calculations, better agreement between experimental and observed values is obtained [11]. Additionally, acetone, along with other LMW carbonyl compounds, can lead to the production of peroxyacetylnitrate (PAN), a reservoir species that allows for long- range transport of NO_x [1] and thus impacts the atmospheric HNO_3 budget. Major sinks of atmospheric acetone are photolysis, oxidation (leading to the production of acetic acid, peroxyacetic acid and methyl glyoxal) and wet deposition [1].

It is not well known whether the oceans are a net source or sink for acetone. Past studies have surmised that the ocean is a net source [3, 12], although more recent studies have obtained data pointing to the contrary [9]. The few reported measurements of acetone in surface seawater show concentrations between 3 and 55 nM [3, 9, 12, 13] with lower concentrations occurring in the bulk water and the higher concentrations occurring in the sea surface microlayer [12]. In the atmosphere the concentration of acetone varies with height and latitude but average mixing ratios are typically 0.3–2.3 ppbv [1, 9, 13].

Acetone quantification in the atmosphere and the oceans is challenging due to its low concentrations and its

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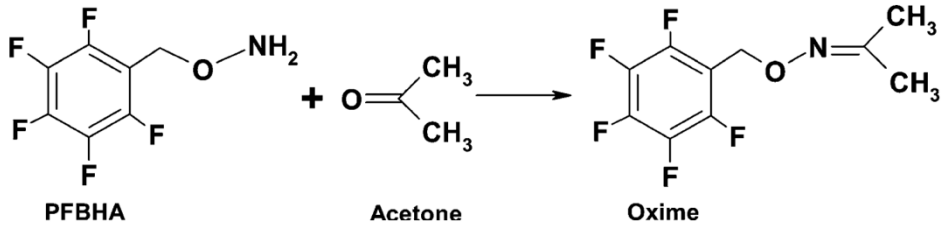
volatility. In recent years, proton transfer reaction mass spectrometry (PTR-MS) [3] and atmospheric pressure chemical ionization mass spectrometry (API-CIMS) [9] have allowed for on-site measurement of acetone in seawater and marine air; however, the instrumentation is expensive and not widely available. Derivatization chromatographic methods are those most frequently found in the literature as they are selective, relatively inexpensive, and widely available. The most commonly reported derivatizing agent for the determination of acetone in both fresh water and seawater is 2,4- dinitrophenylhydrazine (DNPH) [4, 5, 13–16]. The reaction of acetone with DNPH creates a hydrazone, which can be analysed using liquid chromatography (LC) with detection by ultraviolet-visible (UV/Vis) absorbance. Dansyloxyamine (DNSOA) has also been used to derivatize ketones in aqueous samples [17]; the derivatives are separated by LC and quantified by fluorescence. For gas chromatography (GC), derivatization has been accomplished using *O*- (2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) hydrochloride [8, 18–20] (Reaction 3).



(3)

Acetone has also been quantified photometrically by its reaction with vanillin, which produces a yellow-orange dye which absorbs at 430 nm [21], and by its reaction with alkaline salicylaldehyde [22].

DNPH derivatization can provide low detection limits since it is possible to obtain low blank measurements [16]. However, the use of DNPH also limits the separation techniques available due to the decomposition of several hydrazones at higher temperatures [23]. Derivatization using PFBHA results in the formation of an oxime that is amenable to GC since, unlike hydrazones produced by DNPH derivatization, the oximes do not decompose at the high temperature used for GC [24]. Furthermore, the DNPH derivative must be solvent-extracted or otherwise pre-concentrated [16], a step which may be environmentally detrimental (if solvents are needed) or lead to sample contamination.

Solid-phase microextraction (SPME), a method developed by Pawliszyn and co-workers [25, 26], is an attractive alternative for sample preparation, since it requires no solvents and the SPME fibres are readily portable and easy to use. SPME has been used to extract PFBHA derivatives of a range of carbonyl compounds (primarily aldehydes) from both air and water [8, 23, 24].

In the current work, we aimed to develop a routine method for the analysis of acetone in seawater using a SPME-GC-MS technique, which would be sensitive, rapid, facile, environ- mentally benign and use readily available equipment. To date, SPME has been used to a limited extent to analyse acetone in fresh waters only [8] and the present study represents its first published use for seawater. The use of this technique for analysis of selected surface waters from the Nordic seas, taken during the ARK-XX/1 cruise (R.V. *Polarstern*, 2004), is herein presented, and advantages and limitations of the technique are discussed.

Experimental

Materials

Acetone (HPLC grade, 99.5+ %) was purchased from Fisher Scientific (Nepean, ON), and PFBHA hydrochloride from Fluka (St. Louis, MO). Ultrapure water (MilliQ QPAK-1 system, Millipore, Billerica, MA) was used throughout. NaCl was baked overnight at 450 °C to remove any organic contaminants. SPME fibres and holders were purchased from Supelco (Bellefonte, PA). Fibres were initially conditioned as per the supplier's instructions, and re-conditioned daily (15 min, 250 °C) prior to first use.

Glassware was cleaned by rinsing with ultrapure water, followed by baking overnight in a muffle furnace at 450 °C

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to remove organic contaminants. Where this was not possible (e.g. volumetric glassware), it was rinsed with ultrapure water and ethanol and dried overnight at 125 °C.

Solutions, procedure and instrumentation

PFBHA was prepared daily as a 12 mg mL^{-1} (0.0476 M) aqueous solution. Blanks and standard solutions for initial tests were made in 3.5% w/w (0.6 M) NaCl solution to simulate the salinity of seawater. To additionally simulate the buffering capacity of seawater, buffered salt water solutions were made using 34.78 g NaCl, 0.193 g $NaHCO_3$ and 0.026 g HBO_3 per L of solution. This solution was used for calibration purposes (see Results and discussion). Figure 1 shows a schematic of the derivatization and extraction procedure. Derivatizations and extractions were carried out in 20-mL screw-capped vials with Teflon-faced silicone septa. The vials were wrapped in aluminium foil to inhibit any photochemical reactions. Ten-millilitre samples of acetone standards or seawater were used. A 50-µL aliquot of PFBHA solution was added to the vials using an Eppendorf pipette and the samples were derivatized with stirring for 2 h, at which point the septum was pre-pierced with a clean syringe needle, 12.7 µL 0.2 M HCl added if necessary (see Results and discussion) and the SPME fibre was inserted into the vial for 30 min of adsorption. The use of a 30-min adsorption was based on other published studies [8], which indicated that for lower molecular mass PFBHA ketone oximes, maximum adsorption was achieved in 20–50 min, depending on the ketone. Furthermore, it has been shown [27, 28] that as long as the adsorption time is constant, full equilibration of the analyte onto the SPME fibre is not necessary for reproducible quantification.

After solid-phase microextraction, the acetone PFBHA oximes were analysed by gas chromatography/mass spectrometry (GC/MS). The fibre was desorbed (250 °C) in splitless mode for 5 min before the split vent was re-opened. The fibre was then left in the inlet for an additional 10 min to ensure that it was fully clean before re-use. GC- MS (HP 6890 GC with 5973 MSD, Agilent, Palo Alto, CA) was performed on an HP 5-MS (5%-phenyl-methylpolysiloxane) column (30 m× 0.25-mm id× 0.25-µm film) under the following conditions: splitless injection, He carrier gas (1.5 mL min^{-1}, constant flow), injector 250 °C, oven 50 °C for 2 min, then 5 °C min^{-1} to 140 °C, then 20 °C min^{-1} to 260 °C (no final hold), MS in scan mode (*m*/*z* 25–400), with 70 eV electron ionization, transfer line temperature
280 °C, MS source temperature 230 °C, quadrupole temperature 150 °C. The acetone PFBHA oxime was identified by comparison of its mass spectrum with previously published electron ionization mass spectra [18, 29] and in the NIST 5.0 mass spectral database, and by its presence and retention time in the chromatograms of acetone standards. Peaks were autointegrated using HP Chemstation (version B-01.00) software on the total ion chromatograms.

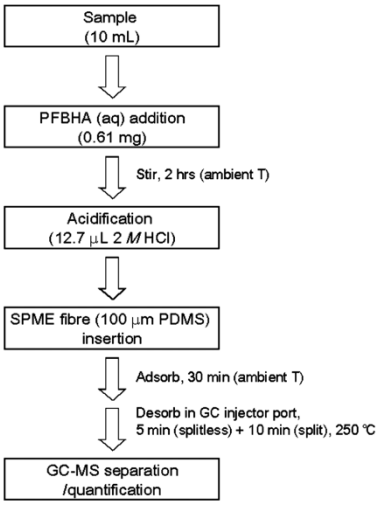

Fig. 1 Schematic of the derivatization/SPME procedure used here for acetone analysis in seawater

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Seawater sampling and analysis

The method was applied to selected samples of surface seawater taken from the Norwegian and Greenland seas during June/July 2004 (cruise ARK-XX/1, RV *Polarstern*). Samples were taken from 11-m depth by means of a direct inlet line in the ship's keel, and were immediately suction- filtered though a 0.22-µm PTFE membrane filter (across a pressure drop of no greater than 300 mbar). Samples were stored frozen in amber glass bottles with Teflon-lined caps (pre-cleaned for EPA Procedure 2 for purgeable volatile organic compounds) (Environmental Sampling and Supply, Oakland, CA) until analysis. Ten-millilitre aliquots of these samples were derivatized and analysed as described previously.

Results and discussion

Figure 2 shows a typical chromatogram and mass spectrum for the analysis of acetone in seawater as its PFBHA oxime. Throughout this study, reported peak areas are from the integration of the total ion chromatogram.

Comparison of SPME fibres (adsorbants)

Derivatized and underivatized acetone were compared on three different SPME fibres: 100-µm polydimethylsiloxane (PDMS), 65-µm polydimethylsiloxane/divinylbenzene (PDMS/DVB), and 75-µm carboxen/polydimethylsiloxane (CAR/PDMS) (Fig. 3a). Underivatized acetone (0.27 µM) was only detected by the CAR/PDMS fibre. The peak for underivatized acetone on this fibre was small and eluted before the split vent had closed, where the baseline of the total ion chromatogram was considerably higher. By comparison, the peak due to the acetone oxime on the CAR/PDMS fibre was larger, exhibited less tailing and eluted later (after the re-opening of the split vent), resulting in more reliable integration. All three fibres detected the acetone oxime at this same concentration (0.27 µM), whereas only the CAR/PDMS fibre detected underivatized acetone. We thus concluded that derivatizing the acetone had the ability to provide a superior method for acetone analysis.

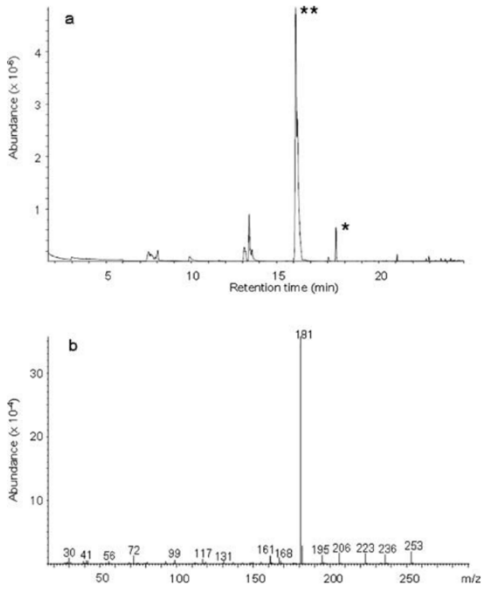

Fig. 2 **a** Typical gas chromatogram of a PFBHA-derivatized seawater sample, showing the acetone PFBHA oxime (*) as well as unreacted PFBHA (**). **b** Mass spectrum of acetone PFBHA oxime peak

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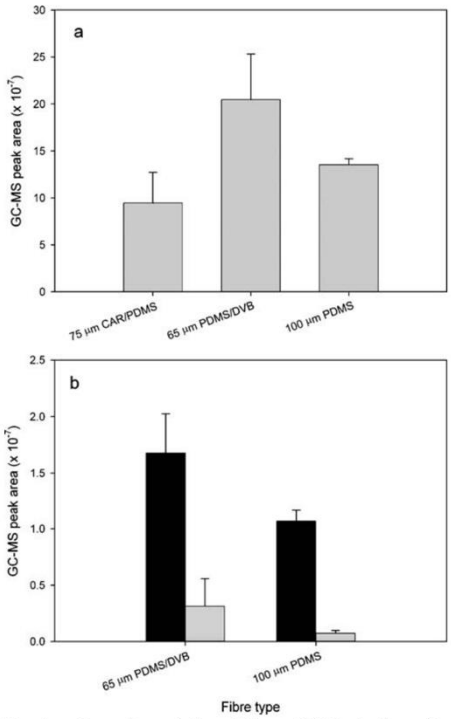

Fig. 3 **a** Comparison of three different SPME adsorbants for sensitivity and reproducibility for acetone PFBHA oxime (0.27 µM acetone), mean±SD, $n=2$. **b** Further comparison of the two best adsorbants in **a**.*Black bars* 67 nM acetone, *grey bars* 13 nM acetone, mean±SD, $n=3$

Figure 3a shows the acetone oxime peak areas on all three fibres, based on duplicate measurements. The measurement on the CAR/PDMS fibre was the least sensitive and least reproducible (34% RSD) and consequently this fibre was not employed in any further experiments. Furthermore, Fig. 3a indicates that the PDMS/DVB fibre shows greater sensitivity while the PDMS fibre shows greater reproducibility under these conditions (0.27 µM acetone, derivatized). Further comparisons between the PDMS/DVB and PDMS fibre were performed, using acetone concentrations of 67 nM and 13 nM, in triplicate. Again, the PDMS fibre showed greater reproducibility and the PDMS/DVB fibre showing better sensitivity (Fig. 3b). The PDMS fibre was thus selected for future experiments owing to its greater reproducibility coupled with its adequate significant sensitivity.

Sample and headspace volume

While the fibre comparisons were done using a sample size of 10 mL, a comparison was performed between 10-mL and 20-mL sample volumes to determine if the headspace had significant effects. For duplicate samples containing 0.34 µM acetone, the blank-corrected acetone oxime peak areas for the two volumes were 5.7% greater for the 20-mL than for the 10-mL sample volume. A 10-mL sample size was used for all other experiments. This smaller sample size reduced the amount of sample and derivatizing agent required while still providing substantial peak areas for acetone analysis.

Effects of pH and buffering in seawater

To determine the optimum pH for the SPME extraction step, the pH of derivatized 34 nM acetone solutions was modified immediately prior to extraction using small quantities of trace metal grade hydrochloric acid (2 M or 0.2 M) or ammonia (0.08 M). These 40- to 50-µL additions changed the volume negligibly. The unmodified solutions of PFBHA and the acetone oxime consistently produced a pH of 3.7±0.1. Over the pH range tested, the pH of the unmodified solution (pH 3.7) was optimal both in terms of peak area and reproducibility (3% RSD) (Fig. 4a), although

the peak areas did not differ greatly over the range studied. This contrasts with the work of Bao et al. [8], who acidified the sample between derivatization and extraction, although they did not explain the purpose of this procedure. Basic pH values were not tested because of the difficulty in obtaining them reproducibly.

It was subsequently noted that the final pH of seawater after derivatization and extraction was between 7 and 8, in contrast to that of salt water standards (pH 3.7, above). This is due to the buffering of seawater by the carbonate and, to some extent borate, systems. Thus, the optimum pH for SPME extraction (pH 3.7) could not be achieved on seawater without modification. We found that the addition of 12.7 μL of 0.2 M HCl brought the pH of seawater and PFBHA to 3.7±0.1 (Table 1), and all seawater samples were therefore acidified this way immediately prior to insertion of the SPME fibre for extraction. For calibration purposes, a buffered salt water was devised (as described in the Experimental section) with which we aimed to replicate the salinity and buffering capacity of seawater. The pH behaviour of this solution on addition of PFBHA·HCl and of 0.2 M HCl was the same as that of natural seawater (Table 1). Tests on seawater from 75.00°N, 16.06°W (site 4, Table 2), derivatized as described previously, demonstrated that the acidification step led to more of the acetone oxime being extracted and detected (Fig. 4b).

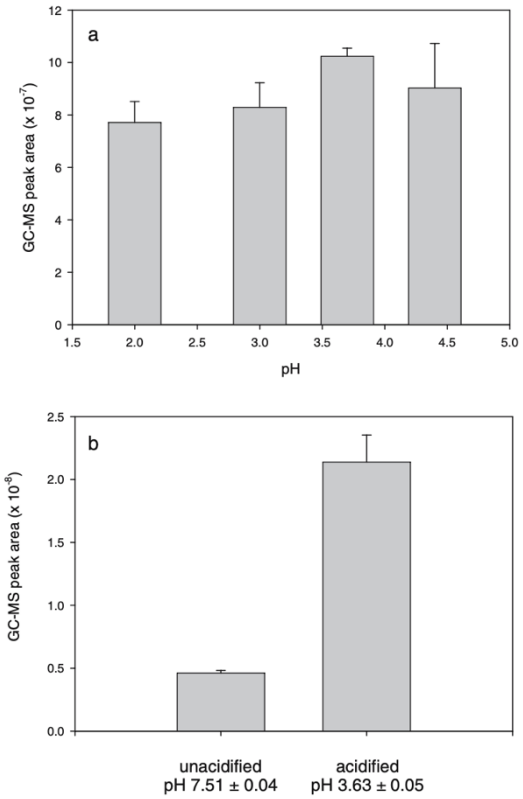

Fig. 4 **a** Effect of pH on the adsorption of acetone PFBHA oxime on a 100 μm PDMS SPME fibre. **b** Effect on seawater (75.00°N, 16.06°W) of acidification prior to SPME extraction. Mean±SD, n=2 (in both plots)

Acetone in salt water blanks

Throughout the experiments described, a notable acetone oxime peak area (1–1.5×10^7 GC-MS peak area counts) was detected in blanks (buffered or unbuffered salt water), as well as in standards and samples. We aimed to identify the source of acetone in these blanks to see if it could be

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Table 1 pH behaviour of surface seawater from 75.00°N, 16.06°W and of the salt water solution buffered by $NaHCO_3$ and HBO_3

	Seawater	Buffered salt water
Original pH	7.83±0.05	7.66±0.05
pH after addition of 50 μL PFBHA solution	7.53±0.07	7.00±0.04
pH after further addition of 12.7 μL 0.2 M HCl solution	3.59±0.08	3.75±0.09

Mean±SD, n=2. The pHs obtained after acidification did not differ significantly at the 5 % confidence level

Table 2 Acetone concentrations in surface waters from selected sites in the Nordic seas

Location, sampling date	Measured [acetone] /nM (mean±SE, n=2)
1. 68.30°N, 9.46°E, 19 June 2006	6.7±3.6
2. 75.00°N, 5.77°E, 25 June 2006	6.3±3.6
3. 75.00°N, 1.80°E, 26 June 2006	9.6±3.6
4. 75.00°N, 16.06°W, 3 July 2006	5.5±3.6
5. 79.34°N, 5.92°W, 12 July 2006	BDL

Location numbers refer to Fig. 7
*BDL*below detection limit

reduced, since method detection limits are currently con- strained by this blank measurement. We considered two possibilities: that acetone in the blanks was coming from the laboratory air during preparation or transfer of standards and samples, or that it was present in the purified water used to make the salt water solutions (and therefore the standards).

On the assumption that the water was the source of this contamination, further purification was attempted. A second purification of the water, already purified as described, was undertaken using a Milli-Q Simplicity 185 water purifier fitted with a Simpak 2 cartridge and a final UV oxidation cell (Millipore, Billerica, MA), and salt water was prepared using this re-purified water. Further batches of salt water solution, prepared using the original (QPAK-1) purified water, were subjected to UV oxidation to attempt to destroy any remaining organic contaminants. Solutions were enclosed in a 3-L cylindrical glass vessel fitted with a 7-cm circular quartz window and irradiated with a 75-W mercury arc lamp ($\lambda \sim \lambda_{max}$ 254 nm; Oriel, Stratford, CT). As a final treatment, the solution and the headspace were sparged/purged with UHP helium prior to irradiation.

Further purification using the Simpak 2 cartridge/final UV oxidation cell did not result in a significantly different (Students' t-test, P<0.05) acetone oxime peak area in the blanks (Fig. 5, a vs. b). Batchwise UV irradiation resulted in higher acetone oxime peak areas in the blanks (Fig. 5, c–e) than in non-irradiated salt water, even after 71 h of irradiation (Fig. 5, d), or after purging/sparging with UHP helium and 17 h of irradiation (Fig. 5, e). These results

suggest de novo formation of acetone from UV oxidation of higher molecular weight contaminants, rather than acetone destruction, although this conclusion is tentative due to limited experimentation.

In an attempt to prevent contamination of samples via laboratory air, the use of acetone anywhere in the laboratory was avoided on days when any of the experiments described in this work were performed. However, to further investigate this air as a potential contamination source, all operations during the preparation, dispensing and derivatization of buffered salt water blanks (except the weighing of the dry salts) were performed in a Plexiglas chamber of ca. 1-m^3 volume with a front face of heavy, flexible, clear polyethylene and flushed with UHP helium, or later, UHP nitrogen. This included enclosing the Milli-Q Simplicity 185 water purifier in the chamber; however, the 2-h stirring and 30-min SPME extraction steps, during which time the samples were isolated from the laboratory atmosphere in vials, were still done on the open bench. In each case, acetone oxime peak areas in buffered salt water solutions prepared in these clean atmospheres did not differ significantly ($P<0.05$) from those in buffered salt water solutions prepared contemporaneously on the laboratory bench. These results suggest that the laboratory air was not the source of traces of acetone in blanks.

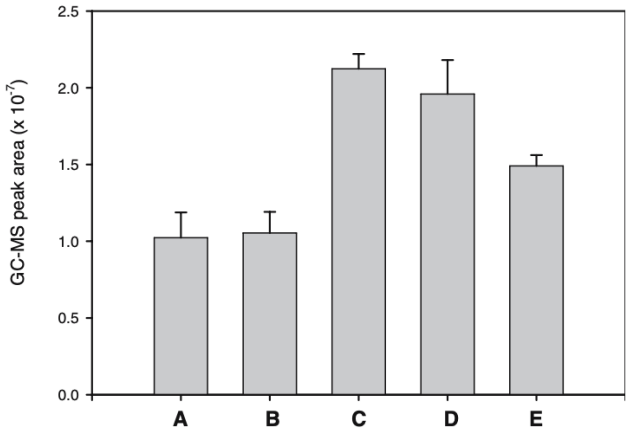

Fig. 5 Acetone PFBHA oxime peak areas in salt water blanks prepared with different purified water sources or irradiated: *A* salt water prepared with milliQ (QPAK-1) water, *B* salt water prepared after further purification of MilliQ water (Simpak 2, UV oxidation), *C* water from *A*, UV-irradiated for 20 h, *D* water from *A*, irradiated for 71 h, *E* water from *A*, sparged with UHP helium and irradiated under helium, 17 h. Mean±SD, $n=2$

Derivatization time

Bao et al. [8] report that, for the PFBHA derivatization of ketones (in contrast to aldehydes) in fresh waters, longer derivatization times (up to 20 h) are needed. Other studies also indicate an increasing yield of PFBHA oximes with longer reaction time for selected ketones, including acetone [18, 19]. We wished to ascertain whether the length of derivatization could be shortened to a more practical time without sacrificing sensitivity and reproducibility, as well as to determine the stability of the acetone PFBHA oxime over time. A series of 10-mL aliquots of surface seawater from 75.00°N, 16.06°W (site 4, Table 2) was derivatized for differing lengths of time before being acidified, adsorbed and analysed as described previously. The peak area from the oxime increased in a near-linear fashion ($r^2= 0.93$) over the first 25 h of derivatization. The increase appeared to continue for up to 66 h, although with more scatter in the data ($r^2= 0.86$); the peak area measured after 68 h was less than that at 66 h. Earlier experiments with acetone standards in NaCl solution had indicated a more rapid degradation or loss of the oxime once 50 h had elapsed. The data suggested that better sensitivity could be obtained using a longer derivatization time, but at a cost of reproducibility, and that sensitivity after a relatively short derivatization time was adequate. Hence, all further samples were derivatized for 2 h.

Calibration

Given previously reported acetone concentrations in sea- water [3, 9, 12, 13], we analyzed calibration standards over

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the range 4.3–150 nM, made in buffered salt water. Calibration samples were analysed with two different SPME fibres of the same type (100-μm PDMS), one for each calibration curve, on separate days (Fig. 6). For both curves, r^2 exceeded 0.99. The two different SPME fibres gave calibration curves with different slopes. This may reflect differences in age and degree of use, and underlines the need to use a single fibre when comparing samples and standards. For the upper calibration curve in Fig. 6, the calculated detection limit (three times the standard deviation of the blank divided by the slope of the calibration curve) was 3.0 nM. This same SPME fibre was used in seawater analysis. Bao et al. [8] reported a detection limit of

1.4 nM for acetone in fresh water by PFBHA derivatization followed by SPME, although that study employed an electron capture detector, highly sensitive to the polyfluorinated derivative, as the GC detector.

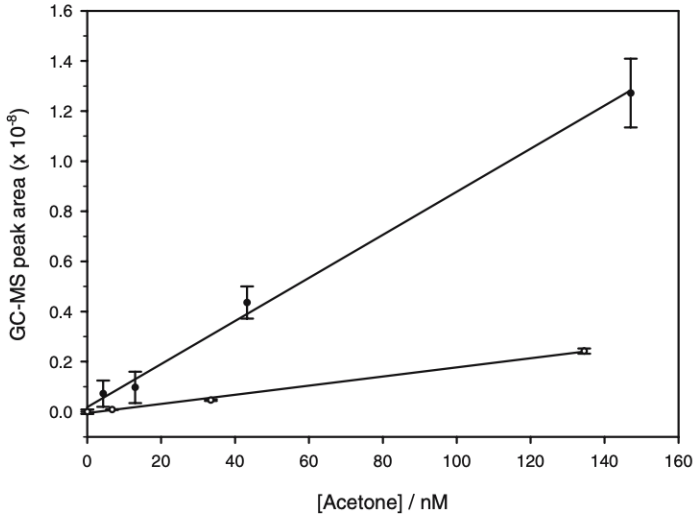

Fig. 6 Calibration curves for acetone, as its PFBHA oxime, using 100-μm PDMS SPME fibres. The *upper* and *lower curves* represent calibrations performed on different days and with different fibres. *Error bars* are standard deviations

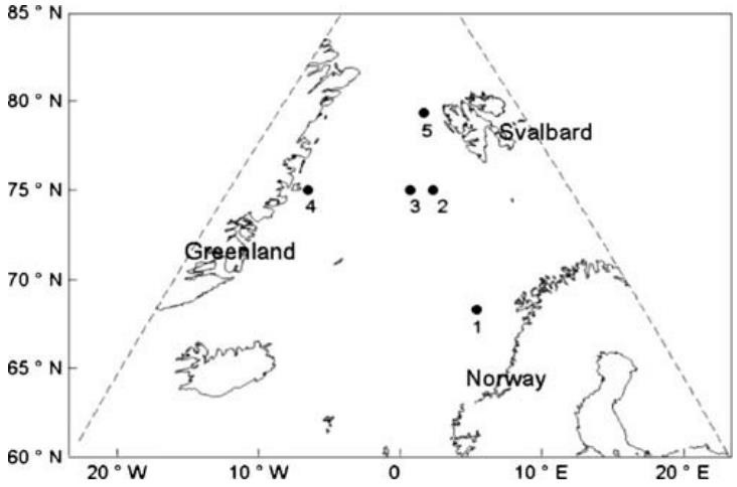

Fig. 7 Sampling locations of seawater samples reported in Table 2. All samples were taken at 11-m depth. Map is a sinusoidal equal-area (Sanson–Flamsteed) projection

Analysis of seawater

Acetone concentrations in selected surface seawater are reported in Table 2, and range from 5.5 to 6.9 nM. These are the first acetone concentrations reported for far North Atlantic and Arctic waters (Fig. 7). They are lower than the mean reported for the tropical Atlantic (17.6 nM) [3], although within the range of values reported from both the Atlantic and Pacific (<3–70 nM) [3, 9, 12]. The values are also surprisingly uniform, given the area covered, and lower than might be expected given that sampling took place during the season of greatest biological activity, that algal blooms were observed in the waters traversed by the cruise at the time of sampling, and that certain marine algal and bacterial species are known to produce acetone [6, 7]. Furthermore, Whelan et al. [6] noted that filtering the sample can lead to additional acetone formation or release. Thus, the reported values must be considered upper limits, and concentrations in these waters may be lower still. Analysis of a greater number of samples from this area should elucidate the degree of uniformity, or patterns of variability, in acetone concentrations. Based on the current data set, it is not yet possible to ascertain whether surface waters of the Nordic seas are a source or sink of tropospheric acetone, especially considering the paucity of atmospheric acetone measurements for these regions and further considering that acetone may be 18 times more concentrated in the sea surface microlayer than in underlying bulk seawater [12].

Conclusions

A variety of factors which affect the SPME analysis of acetone in seawater (SPME adsorbent, pH, derivatization time) have been identified, explored and optimized. While further work is needed to improve detection limits by lowering signals in salt water blanks, results to date indicate a promising, low-cost, easy-to-use method that could be applied to large-scale studies of acetone and other carbonyl compounds in seawater. Initial results from the analysis of North Atlantic/Arctic surface seawater indicate an upper limit of 5.5–9.6 nM acetone in these waters. More extensive analysis of Nordic sea surface waters will better indicate the spatial pattern of acetone concentrations. SPME fibres are readily portable, and no solvents are required. Therefore, through the use of portable GC and/or GC-MS instrumentation (e.g. see refs. [30, 31]) the method could be used at sea, thus avoiding the risk of contamination or artifacts associated with the filtration, transport or storage of seawater samples.

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