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ORIGINAL

Problems Caused by Moisture in Gas Chromatographic Analysis of Headspace SPME Samples of Short-Chain Amines

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Abstract

Volatile amines are usually problematic compounds in sampling, sample pretreatment and gas chromatographic analysis due to their chemical characteristics (polarity, basicity and reactivity). Headspace solid-phase microextraction (SPME) Arrow sampling of aqueous samples were proven to be complicated since moisture in the headspace was also sorbed into the SPME sorbent and resulted in distorted or split peaks for the volatile amines. This was the case especially with old used sorbents not so much with the new ones. Volume of the water sample, sampling conditions, quality of the SPME sorbent and desorption conditions greatly influenced the concentration of water in the headspace and in the sorbent phase. This, in turn, affected the length of the water film in the column which determined the degree of peak splitting and distance between the split amine peaks (water film trapped part of the amine molecules). Addition of the salt to the sample solution and additional drying of the SPME sorbent after the sampling were shown to effectively decrease the amount of water in the headspace and in the sorbent phase. This combined effect of salt addition and drying step resulted in much better peak shapes and intensities for the amines. In the best cases, the peak splitting for the volatile amines could in this way be completely avoided.

Keywords Solid-phase microextraction · Water · Headspace sampling · Volatile amines · Gas chromatography · Split peaks

Introduction

Volatile C_1–C_6 amines are of great concern, for example, in environmental and food analysis. This is due to their significant human-health risks directly (very irritating and corrosive) or via more potent carcinogenic oxidation products (e.g. aminoxides and nitrosamines) [1]. In the environment, amines can originate from industry, combustion, biomass burning, animal husbandry, oceans and, for example, as a carcinogenic chlorination disinfection byproduct dimethylnitrosamine [2]. Several amines are also emitted in CO_2 capture processes [3] where monitoring of these gases will be essential. In addition, soil and vegetation act as sources of amines, especially during periods of high biological activity, and they are believed to have a vital role in atmospheric aerosol formation [4]. Different volatile amines are also emitted as the odorants characteristic for seafood degradation [5, 6]. All this makes their analysis in various sample matrices (air, water, wastewater, food, etc.) necessary. One of the most used analysis techniques for volatile amines is gas chromatography (GC) [7, 8], and also solid-phase microextraction (SPME) have been utilized for sampling of the volatile amines both from the gaseous and liquid samples [7, 9–11].

Analysis of very volatile, polar, reactive and strongly basic amines is problematic especially for GC with SPME, which is usually the main choice of analytical technique. The amino group has a strong interaction with silane groups and siloxane bridges which causes broad distorted peaks and decrease in sensitivity. Amines are also said to decompose in the GC column [12] and they are very likely adsorbed onto the exposed surfaces of the instruments used, vials, injector,

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syringe, sampling lines, etc. To decrease the adsorption, these different surfaces need to be deactivated. Also, the GC column, like the conventional polysiloxane-based columns, need to be deactivated to obtain good peak shapes [13]. This is usually done by base deactivation. Several base deactivated columns for amine analysis are already commercially available [7]. Although with proper columns for amines, bad peak shapes can still be obtained with water matrices [14]. Another approach has been derivatization which can be used to decrease the polarity (also water solubility), to avoid the adsorption problem (both in SPME and GC) and to increase sensitivity [15–18]. Additionally, with derivatization, the volatility can be decreased and retention in GC increased. As an example, Gionfriddo et al. successfully utilized on-fiber derivatization using pentafluorobenzaldehyde (PFBAY) as reagent for determination of short-chain aliphatic amines in aqueous samples by SPME-GC/MS [19].

Solid-phase microextraction (SPME) is a rapid sample preparation technique for chromatographic analysis in the laboratory and especially in the field [20, 21]. In SPME, the analytes (usually volatile and semivolatile organic compounds) are collected on a sorbent material which is generally coated on a small fiber. A recently developed SPME Arrow device has been introduced as an improvement to conventional SPME fiber [22–25]. The main difference between the conventional SPME fiber and SPME Arrow is on the device configuration and sorbent volume [22]. The SPME Arrow is designed to be more rigid and more robust for use in practical work. The stainless steel needle used in SPME Arrow is relatively thick (outer diameter either 1.1 mm or 1.5 mm), whereas the outer diameter of the stainless steel needle used with SPME fibers is typically only 0.58 mm. In the SPME Arrow, the sorbent is coated onto the surface of the inner metal rod that is protected by the outer metal tube. The rod with the sorbent and metal arrow-shape tip can be moved out from the tube to expose (open) and into the tube to cover (close) the SPME Arrow sorbent. Consequently, due to bigger dimensions, the sorbent volume in SPME Arrow is larger than in SPME fiber (ca. 6–20 times), which provides an improvement in sensitivity and capacity.

Generally, the sorbent materials used in the SPME are selected according to the properties of the analytes. Typical sorbent materials used are polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), carboxen (CAR) and carbowax (CW). PDMS and DVB as a hydrophobic material are well suited for the analysis of less polar analytes, whereas the more polar phases should be more appropriate for the polar analytes. For very volatile analytes, the carbon-based adsorbents are working better. Lately, development of different sorbent materials have been the major research topic in SPME [26–29]. Materials for different analytes and sample matrices, as well as optimization of parameters affecting to the extraction, have been widely studied [30, 31]. The effect of water (humidity) has been one of the studied parameters [32–34].

PDMS and other low polarity phases commonly used in SPME are usually considered as hydrophobic and to have low affinity for water. The amount of mobile water in PDMS, for example, have been shown by entropy calculations to be mostly thermally determined and not affected so much by hydrophilic impurities [35]. In addition, water permeation in PDMS has been shown to depend on whether it is in liquid or gas state [36]. Many authors have pointed out that humidity has certain effects on their SPME-GC analysis, and that it must be taken into account in calibration (should be performed at same humidity as the real sample) [12, 37]. For example, a decrease in SPME recovery at higher humidity has been observed for aliphatic amines [12] and acrylamide [38]. No effort has been made to study the effect more closely. In their analysis of amphetamines in urine, Lord and Pawliszyn [39] reported that water was condensed on the needle and that it needed to be positioned in the headspace vial so that only the fiber and its connection tube were below the septum. Also in some cases, bad peak shapes, artefacts and decreased signal intensity were mostly associated to the properties of the amines or other polar analytes and their behavior with active sites in the GC without considering the presence of water [9].

However, in this study, we will more clearly show that some of these problems (peak broadening, bad peak shapes, peak splitting and resulting lower recoveries) associated in the GC analysis of volatile amines can in some cases be related to the relatively large amount of water sorbed by the SPME device and entering the column even from the headspace of the aqueous sample. This was already seen in our earlier paper [23], but is often neglected or not seen with FID or MS with too high a lower *m*/*z* limit in the scan (ion with *m*/*z* 18 not seen). Also with some simple steps, it is possible to reduce the amount of water sorbed by SPME device and thus entering the GC injector and column.

Experimental

Chemicals and Materials

Dimethylamine hydrochloride (DMA, purity 99%) and trimethylamine hydrochloride (TMA, purity 98%) were obtained from Sigma-Aldrich (St. Louis, USA). Diethylamine (DEA, purity ≥ 99.7%) and triethylamine (TEA, purity > 99.5%) were obtained from Fluka (Buchs, Switzerland). Standard stock solutions were done by accurately weighing the pure compounds and diluting them in ultrapure water (Millipore DirectQ-UV, Billerica, MA, USA). Stock solutions at concentrations of 430–2030 mg/L were made monthly and they were stored in the dark at 4 °C. Standard

working solutions were prepared daily by diluting the stock solutions in ultrapure water. Potassium hydroxide pellets and sodium hydroxide pellets were from J.T. Baker (Sweden). Sodium chloride and phosphoric acid (purity 85%) were from Merck KGaA (Darmstadt, Germany). Sulfuric acid (purity 95–97%) was from J.T. Baker (Deventer, Holland) and magnesium sulfate (purity 62–70%) from Fisher Chemicals (Fair Lawn, USA).

Solid-Phase Microextraction

Commercial SPME fiber (PDMS/CAR, 85 µm) was from Supelco (Bellefonte, PA, USA). Commercial SPME Arrows (PDMS/CAR 1000, PDMS/DVB and PDMS) were obtained from CTC Analytics AG, (Zwingen, Switzerland). Coating thickness was 100 µm and coating length 20 mm for PDMS/DVB and PDMS/CAR 1000, whereas it was 250 µm and 15 mm for PDMS. In addition to the commercial coatings, a custom-made SPME Arrow was made using zeolitic imidazolate framework-8 (ZIF-8) as primary extraction phase material. The coating procedure was similar as in the work by Lan et al. [24], with the exception that tetraethyl orthosilicate (TEOS) and PDMS were used as adhesive materials in these prototype custom-made SPME Arrows. Two custom-made SPME Arrows coated with PDMS/TEOS/ZIF-8 sorbent phase (ca. 100 µm thickness and 20 mm length) were prepared. The SPME devices were always conditioned before sampling according to manufacturer's recommendations.

Gas Chromatography–Mass Spectrometry

Agilent 6890N gas chromatograph connected to Agilent 5973N or Agilent 5975C mass selective detector (all from Agilent Technologies, Palo Alto, USA) were used throughout this study. Analytical column used with GC–MS was InertCap column for Amines (30 m × 0.25 mm i.d., GL Sciences, Tokyo, Japan), and it was connected to a deactivated fused silica pre-column (1.0 m × 0.53 mm) with a glass press-fit connector (BGB Analytik, Böckten, Switzerland). Helium (99.996%, AGA, Espoo, Finland) was used as carrier gas in a constant pressure mode (90 kPa). The injector (desorption) temperature was 250 °C. The SPME Arrows were desorbed in splitless mode (2 min) using a 2.0 mm i.d. split/splitless liner together with a standard inlet septum. Conventional SPME fibers were desorbed in splitless mode using a 0.75 mm i.d. splitless liner. Merlin Microseal (23 gauge) septum replacement and a Merlin nut (Merlin Instrument Company, Half Moon Bay, USA) were employed in the injection port when working with the SPME fibers. Desorption time was either 30 or 40 s. Oven temperature program was from 40 °C (5 min) to 250 °C (4 min) at 30 °C/min. Electron ionization (70 eV) was used in MS with a scan range of *m*/*z* 30–300 which was later changed to *m*/*z* 15–300 to detect the water peak. GC–MS interface temperature was kept at 250 °C.

Sample Preparation

The sample preparation and SPME procedure used are presented in detail elsewhere [23]. Briefly, the general extraction procedure was as follows: amine standard solution (1–5 mL) was pipetted into a 20 mL headspace vial, which was instantly sealed with a PTFE/silicone septum screw-cap. Potassium hydroxide solution (5 M) was added into the sample solution to neutralize the amines and to promote their partitioning into the headspace. The solution was stirred for 5–10 min at 1400 rpm rate before HS-SPME. The experiments conducted were qualitative in nature and done by following a trial-and-error approach. Drying procedure after the SPME, as will be explained later on, was tested with different drying agents (KOH pellets, NaOH pellets, $MgSO_4$, H_2SO_4) placed into a separate 20 mL headspace vial. The SPME sorbent was exposed inside the headspace of the vial containing the drying agent. The SPME sorbent was not in direct contact with the drying agent. The drying procedure relied on the hygroscopicity of the drying agent to remove the loosely sorbed water from the SPME Arrow sorbent material (or from the surfaces of the SPME Arrow device).

Results and Discussion

Problem of Duplicate Amine Peaks

During the development of a headspace SPME Arrow-GC–MS method for volatile amines, a second peak for the amine studied (dimethylamine, DMA) with a longer retention time appeared in the chromatograms with identical mass spectra (Fig. 1) [23]. This second peak was becoming larger with the time the SPME material (SPME Arrow with PDMS/CAR 1000) was used repeatedly in the experiments (black trace in Fig. 1). Inspection of the used old SPME Arrow PDMS/CAR 1000 revealed that about 10–15% of the sorbent had been lost. Most likely wearing and damaging of the sorbent material was at least partly responsible for the appearance and increase of the second peak of dimethylamine. However, other commercial SPME Arrow materials (not damaged ones) also produced the second peak for dimethylamine, whereas SPME fiber showed only one broad peak at the correct retention time (Fig. 1). Also, as seen in the figure, the nonpolar PDMS phase showed a much smaller second peak for DMA with shorter retention time. It seems that a more polar and porous sorbent phase and the use of SPME Arrow instead of SPME fiber makes this duplicate peak phenomena more serious. Both larger amount of the

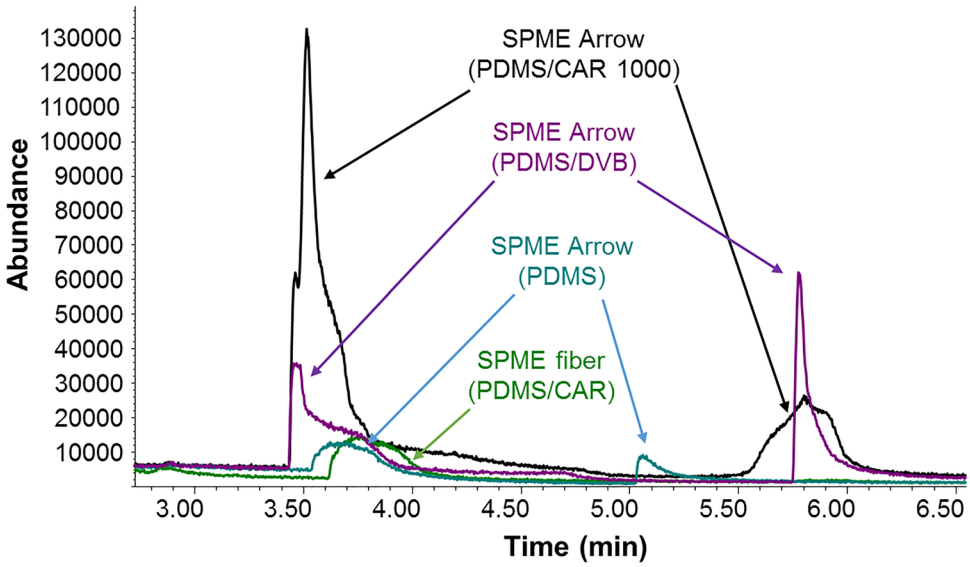

Fig. 1 Overlaid GC–MS extracted ion (*m*/*z* 44) chromatograms of dimethylamine when different SPME devices and sorbents (marked in the plot) were used for extraction. Extraction conditions: 5 mL of 1 mg/L DMA solution and 60 min extraction time under 1400 rpm stirring rate

sorbent and the larger metallic surface area in SPME Arrow could be the reason for this. However, this issue was more carefully studied.

To verify that the duplicate peaks of amines was not an instrument-related problem, the most obvious GC parts were cleaned or replaced. For example, both the pre-column and analytical column were replaced with new ones, GC inlet liner was cleaned, septum replaced and the GC setup was thermally conditioned overnight. None of these steps helped to prevent the appearance of duplicate amine peak. Once instrument-related problem was tentatively ruled out, it was considered that the problem must be caused by some other aspect in the extraction process.

Effect of Conditions to the Problem

First of all, no second peak of amines was observed with a gas-tight syringe injection from the headspace of the sample vial (data not shown). Second, when the sample vial contained only gaseous DMA (no aqueous sample solution inside the vial), only one peak for DMA was obtained at the correct retention time when different SPME Arrows were used for extraction (Fig. 2, green traces). However, when the sample vial contained an aqueous sample solution, a second peak for the DMA was seen (Fig. 2, black traces). Similar results were also observed with the other amines (DEA, TEA) tested. Chromatograms with duplicate peaks for DEA and TEA are shown in Fig. S1 with commercial SPME Arrows (PDMS/DVB and PDMS/CAR 1000) used for the extraction from a vial containing aqueous sample solution. It is worth noticing, that the time difference between the two peaks is much shorter with the less volatile DEA and TEA (compare Fig. 1 and S1). No duplicate amine peaks were observed when the extractions were done from a vial containing only gaseous DEA or TEA (Fig. S2).

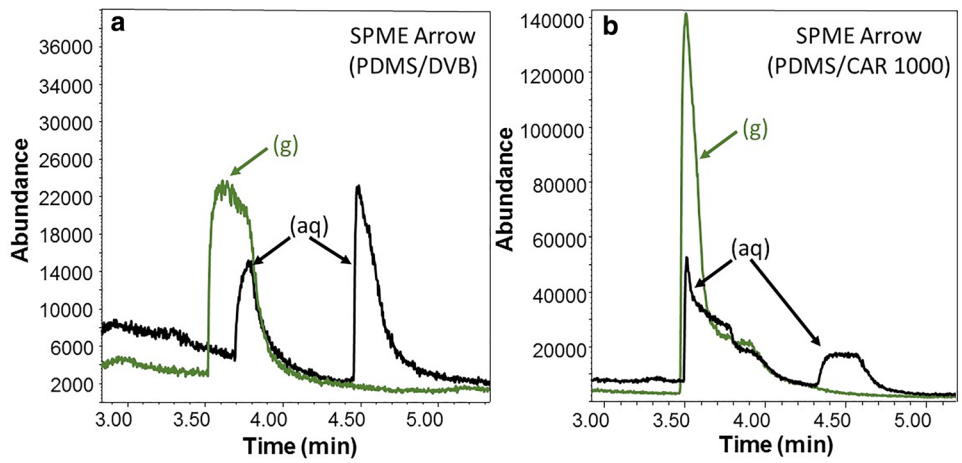

Fig. 2 GC–MS extracted ion (*m*/*z* 44) chromatograms of DMA sampled with HS-SPME Arrow from the 20 mL headspace vial at room temperature using **a** PDMS/DVB and **b** damaged PDMS/CAR 1000 for the extraction. Gaseous DMA (**c** ≈ 2 mg/L) with no aqueous solution (green traces) and 1 mL of aqueous DMA solution (**c** = 1 mg/L) inside the vial (black traces)

The most severe peak splitting of amines was observed when the custom-made SPME Arrow (PDMS/TEOS/ZIF-8) was used for extraction. This coating material stability was relatively poor and the coating surface became visibly uneven after multiple extraction/desorption cycles. Nevertheless, this custom-made SPME Arrow provided valuable information about the peak splitting phenomena. The effect of desorption temperature was examined with the custom-made SPME Arrow as shown in Fig. S3. Changing the desorption temperature from 200 to 250 °C increased the first DMA peak intensity while its retention time remained the same (Fig. S3). At the same time, the later eluting second peak size was also increased and the retention time was decreased (Fig. S3). With the same SPME Arrow, the extraction temperature effect on the second peak was also studied (Fig. 3). As can be seen, the second peak retention time and size were greatly increased with the extraction temperature. Extraction temperature effect was seen in our earlier paper with SPME Arrow PDMS/CAR 1000 [23], and also the decrease in recovery by the resulting higher humidity at higher extraction temperature seen by Namieśnik et al. [12] can be explained by this.

All this can be explained by the water retained by the SPME device and desorbed into the column. At the beginning of the GC run, the vaporized water will be condensed inside the column and act as a solvent trap for part of the amine molecules (most of the volatile amine is vaporized and eluted out normally in the first peak). The trapped amine is released as a second peak after all water is vaporized and eluted out from the column. This also explains the large variability in size and retention time of the second peak since the SPME and analyte characteristics together with extraction and desorption conditions all affect the appearance of the second peak. It also explains the effect of the desorption temperature since higher desorption temperature will cause water to come through the column faster and larger portion of the amine to be in the first peak. In addition, a higher extraction temperature results in a greater amount of water being present in the headspace that can be sorbed by the SPME. This is seen as a longer retention of the second peak as it takes longer time for a larger amount of water to come out from the column.

To verify this reasoning, the MS scan lower *m*/*z* limit was set to *m*/*z* 15 to monitor the water peak (based on *m*/*z* 18). We then repeated some of the experiments done earlier to see also the size of the water peak. Also, a new SPME Arrow coated with PDMS/CAR 1000 was compared to the previously used damaged SPME Arrow coated with the same sorbent material. The initially used HS-SPME Arrow-GC–MS method was applied with both of these SPME Arrows. As can be seen in Fig. 4, with the damaged SPME Arrow (Fig. 4a) the size of the water peak is much larger than with the undamaged SPME Arrow (Fig. 4b). Only one DMA peak was observed with the new undamaged SPME Arrow, whereas duplicate DMA peaks were observed with the old damaged SPME Arrow. The second peak of DMA is eluting right after water has eluted from the column, indicating that part of DMA is indeed being trapped/interacting with the condensed water inside the column (Fig. 4a). This phenomena was even more pronounced with the custom-made SPME Arrow (Fig. S4).

There were no clear difference observed (data not shown) on the water peak size (width) without DMA and with DMA using various SPME Arrow sorbent phases (PDMS, PDMS/CAR 1000, PDMS/DVB). Overall, DMA is not necessarily attracting much more water onto the Arrow coating, except if the coating is damaged like in the case of PDMS/TEOS/ZIF-8, where the water peak width was 3.4 min without DMA and with DMA it was 4 min.

In view of these results presented above, a few additional experiments were performed wherein solely the amount of water was being monitored. Different sorbent coated SPME Arrows and a blank uncoated SPME Arrow were exposed inside an empty headspace vial. The older SPME Arrows showed larger water peaks than the new SPME Arrow and the uncoated blank SPME Arrow (Fig. 5a). The water peak width was slightly smaller with the new PDMS/CAR 1000 than with the uncoated Arrow (Fig. 5a). Figure 5b clearly

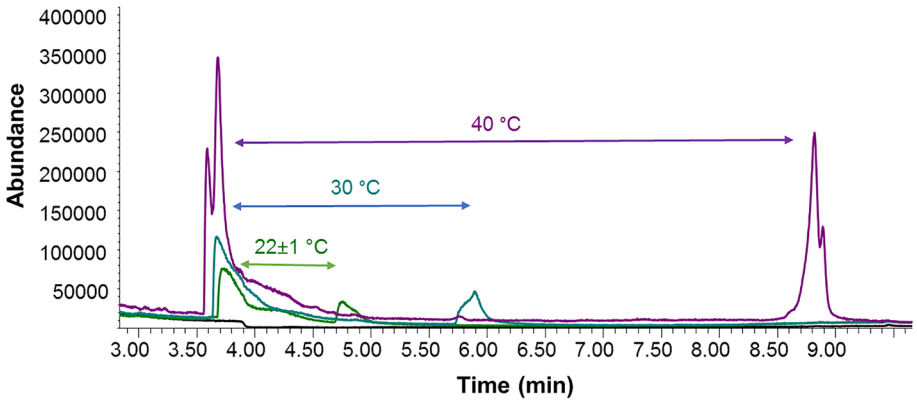

Fig. 3 GC–MS extracted ion (*m*/*z* 44) chromatograms of dimethylamine (DMA) sampled 30 min with custom-made SPME Arrow (PDMS/TEOS/ZIF-8) from the 20 mL headspace vial at different extraction temperatures. MS spectra of these peaks were identical (data not shown)

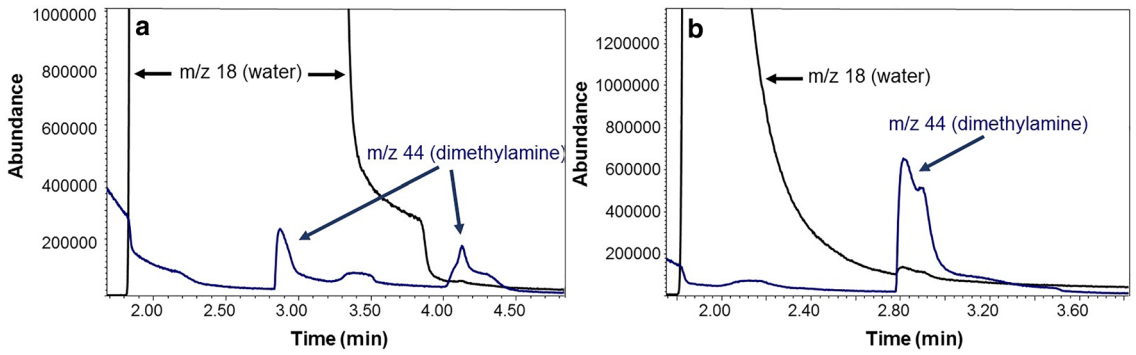

Fig. 4 Overlaid extracted GC–MS ion chromatograms (*m/z* 18 and *m/z* 44) to show water and DMA peaks. **a** Old damaged SPME Arrow (PDMS/CAR 1000) with 5 mL aqueous DMA solution (1 mg/L) in 20 mL headspace vial. **b** Same with a new undamaged SPME Arrow (PDMS/CAR 1000). Extraction for 45 min at room temperature and no stirring

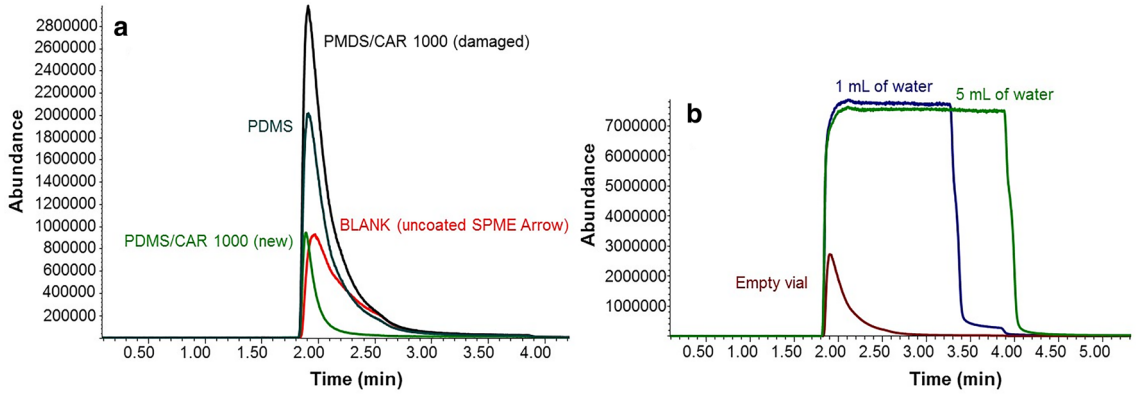

Fig. 5 Overlaid extracted ion GC–MS chromatograms (m/z 18) **a** with the old and new CAR 1000 SPME arrows, with PDMS Arrow and with uncoated arrow (blank) from the empty 20 mL headspace vial. **b** Same with the old SPME CAR 1000 arrow (from the headspace) with different amounts of water in the 20 mL headspace sample vial. Extraction time was 30 min and two repetitions were done with each Arrow

shows the large difference between empty extraction vial and that containing some water solution. The water peak obtained after headspace sampling is even wider the greater was the water volume (Fig. 5b). This explains why previously only one amine peak was observed, when the extraction was performed from a vial containing only gaseous amine (Fig. 2 and S2).

Summary of Observations and Considerations

Based on the experiments presented above, it is obvious that water is at least partially causing the problem of the duplicate amine peaks. However, it is somewhat surprising that even at room temperature extraction conditions, there is such a large amount of water retained into the SPME Arrow that this causes the amine peaks to split. It seemed that the more porous the sorbent material was and the more uneven the bulk sorbent surface was, the more water was sorbed into the SPME Arrow (e.g. Figs. 1, 5a). This may be partly explained by the damaged (some sorbent stripped away and metal surface exposed) and possibly contaminated coating. Sorbent surface can, for example, contain metal particles as impurities originating from the metal parts of the SPME Arrow similarly as was found for SPME fiber by Haberhauer-Troyer et al. [40]. These impurities can partly be responsible for the increase in water sorption and explain the resulting lower SPME extraction efficiency observed also by others [33]. Compared to SPME fiber, SPME Arrow contains more metal surfaces (the metal tip of the SPME Arrow and at least partly the outer tube covering the sorbent) that are in the contact with the headspace of the sample and can be responsible for water sorption. However, it cannot be excluded that, e.g. the custom-made SPME Arrow sorbent had some physicochemical characteristics, which were additionally responsible for the duplicate peak problem. Nonetheless, this custom-made SPME Arrow is a special case among the other commercial coatings tested in this study and should be evaluated with caution.

Solutions to the Water Problem

First of all, it is important to notice that the solvent conditioning of the PDMS/DVB Arrow with methanol before the extraction was seen to effectively decrease the amount of the water in the Arrow at least to one-third of the original (data not shown). The DMA still produced split peaks but they were much closer to each other near the first peak retention time, whereas most of the DMA eluted in the area of the second peak without methanol conditioning. This indicates that similar to the SPME fibers also the SPME Arrow need to be properly preconditioned.

In principle, there are few fundamentally different approaches to solve the water problem. One approach is to adjust the GC–MS conditions in such a way, that the effect of water interacting with the amine compounds inside the column is reduced. This can be accomplished by, e.g. increasing the initial GC oven temperature. Increase in GC column initial temperature shortened the water peak (long tail will remain) and the distance between the duplicate DMA peaks (Figs. S5 and S6). However, at high starting temperatures, the DMA peak broadened greatly. Although it seems that the 80 °C temperature would be optimal in decreasing the water re-condensation and avoiding the DMA peak splitting (Fig. S6), the retention and separation between different volatile amines (DMA, EA and TMA) will unfortunately be lost making this approach unpractical. Alternatively, instead of using splitless injection, split mode desorption could be used, which likely would reduce the peak splitting phenomena [8], however, sensitivity would also be decreased.

Another approach to solve the water-induced problem would be to get rid of the water prior to GC analysis. This was first attempted by applying different drying procedures after the extraction and before the desorption step. Preliminary trials were done using either KOH pellets as drying agent or N_2 gas flow for the drying (see Fig. S7). Both drying procedures reduced significantly the amount of water entering the column and only one dimethylamine peak was observed in the chromatograms after the drying steps (Fig. 6). DMA peak areas were also larger than the total sum of the duplicate peaks (Fig. 6). These results were promising, since they indicated that the amount of water is efficiently reduced and apparently no dimethylamine is lost during the separate drying step. However, it is possible that dimethylamine could also equilibrate back into the gas phase and partly lost during this drying step. This was not noticed or studied here, but could be verified with more accurate quantitative measurements.

The performance of different drying agents and amounts were further tested using the custom-made SPME Arrow for extraction. This SPME Arrow had the worst performance and the greatest amount of water retained into it (Fig. S4), thus it provided valuable information about the effectiveness of the different drying agents. Only minor differences between the different drying agents (KOH, NaOH, H_2SO_4 and $MgSO_4$) tested were obtained in terms of the amount of water detected after the drying step (Fig. S8). Even though the amount of water was significantly reduced after the drying (Fig. S8), duplicate dimethylamine peaks were still observed when the custom-made SPME Arrow was utilized. Of the different drying agents tested, $MgSO_4$ was the least efficient while the other ones provided similar results, KOH pellets being the most repeatable one. Compromise between the amount of water and the drying time needs to be considered since only a small improvement can be obtained by extending the drying time from 5 min to 20 or even 40 min. A similar effect can be achieved more easily by increasing the amount of drying agent (Fig. S8).

Second option to decrease water amount in the HS-SPME method is a salt addition to the sample solution. When NaCl salt is added to the solution, the relative humidity in headspace should be reduced. Saturated 36% (w/w) solution in

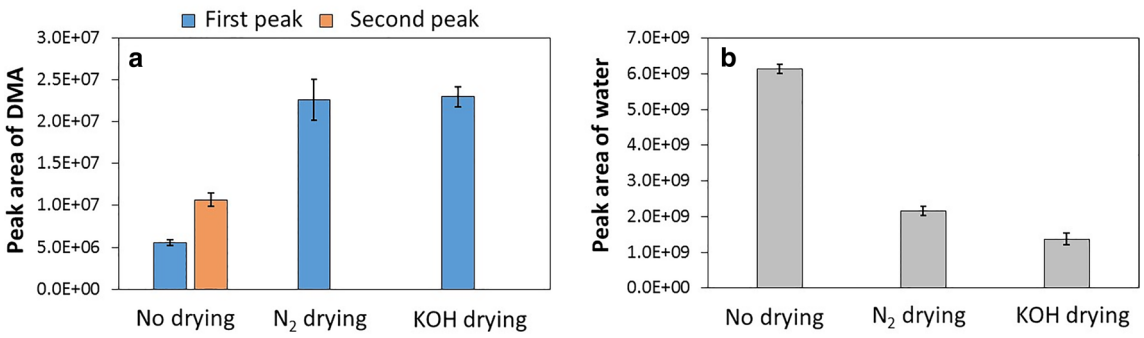

Fig. 6 The effect of different drying approaches on the amount of **a** dimethylamine and **b** water detected. The damaged SPME Arrow PDMS/CAR 1000 was used for the extraction. Extraction conditions: sample volume 5 mL, DMA concentration 1 mg/L, 250 µL of 5 M KOH added and 30 min extraction time. Drying time used with both N_2 purge and KOH pellets was 5 min. Error bars represent the repeatability of duplicate measurements

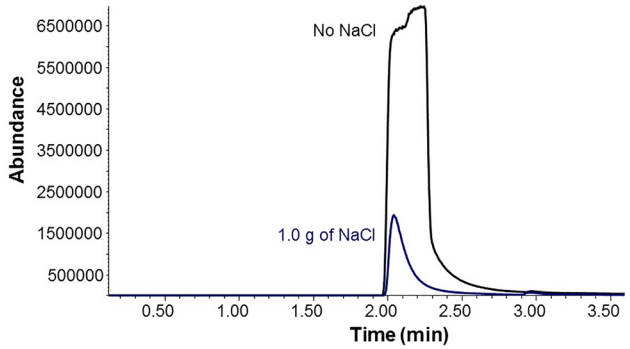

Fig. 7 Effect of salt addition to the water peak size (*m/z* 18) with SPME Arrow (undamaged PDMS/CAR 1000). Extraction for 30 min without salt and with 1.0 g of NaCl added into 5 mL solution

room temperature should result in relative humidity of 75.5% and in this way it could be controlled [41]. Figure 7 clearly shows how well the salt addition of 1 g already decreases the water peak size compared to a situation without any salt added. With the larger water peak produced by the custom-made PDMS/TEOS/ZIF-8 SPME Arrow sorbent (Fig. S9), it is clearly visible that the smallest (optimal) water peak is obtained with saturated solution (between 1.5 and 2 g NaCl added). In addition, the amine peak splitting is finally then avoided even with this custom-made SPME Arrow.

Finally, the importance and effect of the combined KOH drying step and NaCl addition is illustrated in Fig. 8. As can be seen, additional drying step is required with this custom-made SPME Arrow even though the salt addition already helps to reduce the size of the water peak significantly (Fig. 8 and S9). However, there was still a larger amount of water left in this custom-made SPME Arrow when compared to the commercial SPME Arrows.

Conclusions

Water was shown to be retained by the SPME Arrow at higher quantities than expected from the headspace of the aqueous sample. This caused bad chromatographic peak shapes and severe peak splitting for the volatile amines. Peak splitting was due to the solvent trapping caused by the re-condensing water in the column, thus making part of the amine come out later from the column. A drying procedure was introduced to reduce the water amount and to avoid the peak splitting problem. The amount of water entering the SPME adsorbent could most effectively be minimized by controlling the relative humidity inside the sample vial via salt addition into the sample solution and using a separate drying step prior to desorption. The salt addition and drying step could be implemented as part of the SPME method especially in qualitative and semiquantitative measurements to improve the chromatographic peak shapes and to extend the applicability of the SPME especially in the case of very volatile and water-soluble analytes. These steps should be considered when aqueous samples or gaseous samples with high humidity need to be analysed.

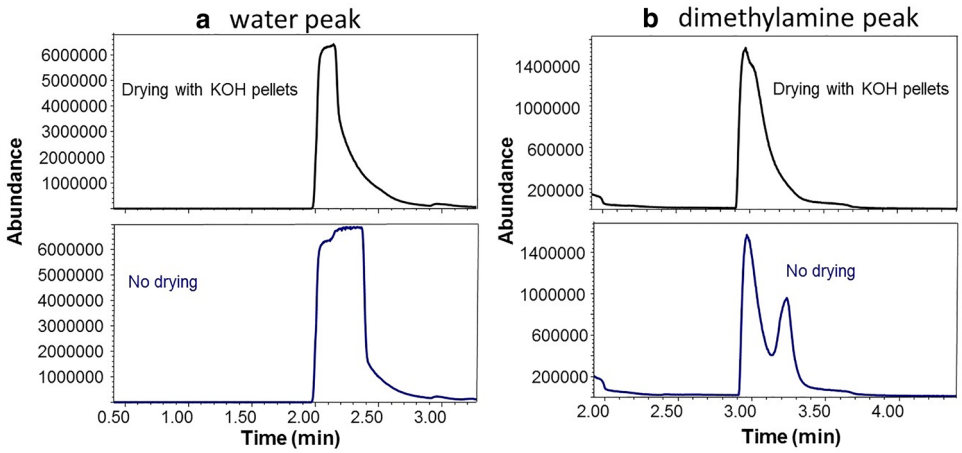

Fig. 8 GC–MS extracted ion chromatograms of **a** water (*m/z* 18) and **b** dimethylamine (*m/z* 44) when the custom-made SPME Arrow (PDMS/TEOS/ZIF-8) was used in extraction experiments using only NaCl (lower chromatograms) and both NaCl and KOH drying (upper chromatograms) to reduce the amount of sorbed water. Extraction conditions: sample volume 5 mL, DMA concentration 1 mg/L, 250 µL of 5 M KOH added, 2.0 g of NaCl added and 30 min extraction time. Drying step: 5 min drying time with 2.6 g of KOH-pellets inside a vial prior to GC–MS analysis

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Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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