Modified zeolitic imidazolate framework-8 as solid-phase microextraction Arrow coating for sampling of amines in wastewater and food samples followed by gas chromatography-mass spectrometry

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Abstract

In this study, a novel solid phase microextration (SPME) Arrow was prepared for the sampling of volatile low molecular weight alkylamines (trimethylamine (TMA) and triethylamine (TEA)) in wastewater, salmon and mushroom samples before gas chromatographic separation with mass spectrometer as detector. Acidified zeolitic imidazolate framework-8 (A-ZIF-8) was utilized as adsorbent and poly(vinyl chloride) (PVC) as the adhesive. The custom SPME Arrow was fabricated via a physical adhesion: (1) ZIF-8 particles were suspended in a mixture of tetrahydrofuran (THF) and PVC to form a homogeneous suspension, (2) a non-coated stainless steel SPME Arrow was dipped in the ZIF-8/PVC suspension for several times to obtain a uniform and thick coating, (3) the pore size of ZIF-8 was modified by headspace exposure to hydrochloric acid in order to increase the extraction efficiency for amines. The effect of ZIF-8 concentration in PVC solution, dipping cycles and aging temperature on extraction efficiency was investigated. In addition, sampling parameters such as NaCl concentration, sample volume, extraction time, potassium hydroxide concentration, desorption temperature and desorption time were optimized. The Arrow-to-Arrow reproducibilities (RSDs) for five ZIF-8 coated Arrows were 15.6% and 13.3% for TMA and TEA, respectively. The extraction with A-ZIF-8/PVC Arrow was highly reproducible for at least 130 cycles without noticeable decrease of performance (RSD<12.5%). Headspace SPME of 7.5 mL sample solution with the fabricated ZIF-8 coated Arrow achieved linear ranges of 1-200 ng mL^{-1} for both TMA and TEA. The limit of quantitation (LOQ) was 1 ng mL^{-1} for both TMA and TEA. The method was successfully applied to the determination of TMA and TEA in wastewater, salmon and mushroom samples giving satisfactory selectivity towards the studied amines.

Keywords: Acidified Zeolitic Imidazolate Framework-8; Amines; Food; Gas Chromatography-Mass Spectrometry; Solid Phase Microextraction Arrow; Wastewater

1. Introduction

Solid phase microextraction (SPME) was introduced by Pawliszyn and his co-workers in 1990s.[1] It is a simple, time-saving, environmentally friendly and solventless non-exhaustive sampling technique, which integrates sampling and sample preparation in one step.[2] Conventional SPME fiber comprises of a fused silica fiber wrapped with the sorbent material, such as polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), carbowax (CW), carboxen (CAR), polyethylene glycol (PEG), templated resin (CW/TPR) and their composite materials.[3] In the last two decades, SPME has been extensively used for the determination of volatile, semi-volatile and non-volatile, nonpolar and polar compounds in environmental,[2] biogenic [4] and food [5-7] samples with both headspace (HS) and direct insertion extraction (DI-SPME) modes.

SPME Arrow is a recent development of SPME and has been successfully exploited in the determination of amines and polycyclic aromatic hydrocarbons (PAHs.) [8, 9] There are already many coatings commercially available for SPME Arrow such as PDMS/Carboxen-1000, PDMS/Carboxen-WR and PDMS. SPME Arrow has large sorbent volume, which increases sample capacity and efficiency of the extraction. Moreover, its design makes it resistant during manipulation and less likely to core the inlet septum in gas chromatograph.

In recent decades, amines as widespread pollutant compounds in the environment have drawn extensive scientific, societal and political attention due to their toxic, carcinogenic and bioaccumulation characteristics.[10] Moreover, their importance in atmospheric chemistry and effect on global climate has been shown.[11] Because of the increasing use in human activities, such as farming and industry, amines should be monitored, especially in densely populated areas. In addition, amines are good food safety markers, especially for fish.[12] Thus, sensitive method for their determination in biological matrices is needed. Unfortunately amines are challenging compounds to

be analyzed due to their volatility and high polarity, which make them difficult to separate from sample matrices.

Amines have been analyzed in environmental [13-16], biological [17] and food [18-21] samples using a variety of sampling techniques, such as: SPME [15-17, 22], liquid–liquid–liquid microextraction (LLLME) [13, 14, 18], solid phase extraction (SPE) [19-21] and many analytical techniques including gas chromatography (GC) coupled with different detectors, high performance liquid chromatography (HPLC) and capillary electrophoresis (CE) [23]. SPME has been recognized as the extraction method of choice in a wide variety of analyses with different sample matrices, and GC-MS has been commonly used in the analysis of volatile amines due to its simplicity, good sensitivity and relatively short analysis time. In our previous work, a series of SPME fibers and SPME Arrows with various coating materials were employed for the HS-SPME of dimethylamine and trimethylamine that were analyzed by GC-MS.[8] Carbon-based porous particle material, Carboxen-1000 with a pore size around 1 nm exhibited the best extraction capacity to these two amines in HS-SPME mode for air and wastewater samples. The results achieved encouraged us to evaluate further the performance of other porous materials for the extraction of volatile amines.

Metal organic frameworks (MOFs) have been widely utilized due to their attractive properties such as the possibility of pore size modification, large surface area, micro-porosity, and good thermal stability.[24-26] However, many MOFs are very sensitive to water as their metal-oxygen bonds can easily be degraded by even a small amount of moisture.[25] Zeolite imidazolate frameworks (ZIFs) are a relatively new class of water-stable frameworks and they have been utilized for pre-treatment of aqueous sample because of stronger metal-ligand bonds and hydrophobicity.[26] ZIF-8 has become one of the most studied ZIF materials because it does not only possess the MOFs original properties but also has exceptional thermal and chemical stability in both water and alkaline solutions.[27] All of the advantages mentioned above attracted us to investigate the potential application of ZIF-8 as a high-efficiency sorbent for the extraction and preconcentration of analytes from the aqueous phase.

In this study our goal was to develop a new hydrophobic ZIF-8 based SPME Arrow using PVC as adhesive with dipping method. To increase the extraction capacity of volatile amines, the pore size of ZIF-8 was modified by hydrochloric acid. The acidified-ZIF-8 SPME Arrow together with GC-MS analysis was evaluated for the determination of trimethylamine (TMA) and triethlylamine (TEA) in wastewater, salmon and mushroom samples. The results were compared with those achieved with a previously optimized method based on PDMS/Carboxen-1000 Arrow.

2. Experimental

2.1. Chemicals and materials

Trichloroacetic acid (≥99.5%), tetrahydrofuran (THF) (≥99.9%), methanol (≥99.9%), zeolitic imidazolate framework-8 (ZIF-8), poly(vinyl chloride) (PVC), trimethylamine hydrochloride (TMA·HCl, 98%) and triethylamine hydrochloride (TEA·HCl, ≥99.0%) were purchased from Sigma-Aldrich (St. Louis, USA). Sodium chloride (NaCl) was purchased from Fisher Scientific (Loughborough, Leics, UK). Hydrochloric acid (HCl) (both 0.1 and 1 M) and sodium hydroxide (NaOH) (0.1 M) were purchased from Oy FF-Chemicals Ab (Haukipudas, Finland). Potassium hydroxide (KOH) was purchased from VWR Chemicals (Pennsylvania, USA). Perchloric acid ($HClO_4$) was from Merck (Darmstadt, Germany). Ultrapure water from the water purification system (Millipore DirectQ-UV, Billerica, MA, USA) was used for stock, standard, and sample solution preparation. Individual stock solutions of TMA and TEA were prepared in ultrapure water at a concentration of 1000 mg L^{-1} and stored at 4 °C in the refrigerator.

2.2. Preparation of ZIF-8/PVC coated SPME Arrow

The ZIF-8 solution was prepared as follows: 1 mL of THF was added into a 2 mL plastic tube, then 10 mg of PVC was added and the mixture was shaken on an IKA Electronic VIBRAX-VXR shaker (Breslau, Germany) 1200 rpm for 10 min. 60 mg of ZIF-8 particles were then added to the mixture

and shaken at 1200 rpm for 15 minutes. Finally, a viscous white ZIF-8/PVC/THF suspension was obtained.

The preparation schematic of ZIF-8 coated Arrow is shown in Figure 1. An uncoated SPME Arrow was first washed by sonication in 10 mL methanol, followed by 10 mL NaOH (15 minutes each) and rinsed three times with ultrapure water. Then, Arrow was etched by immersion into 10 mL of 0.1 M HCl for 1 hour in order to increase the Arrow surface area. After that, Arrow was washed three times with ultrapure water and dried at room temperature.

The etched Arrow was immersed into ZIF-8/PVC/THF suspension for 10 seconds and pulled out slowly during several seconds. Then Arrow was heated to 200 ºC in an oven for 15 minutes to remove THF. This cycle was repeated up to five times.

Aging of the ZIF-8/PVC Arrow was carried out in the GC injection port with helium (99.996%, AGA, Espoo, Finland) as the carrier gas in order to eliminate reduced residual impurities. The temperature was 250 ºC and the aging time was 60 minutes.

Finally, the aged ZIF-8/PVC Arrow was exposed for 1 hour to 10 mL of 1 M HCl solution in a 20 mL headspace vial equipped with a PTFE/silicone septum screw-cap. Then vial was heated to 50 ºC in a heating block. Headspace acidification was chosen to avoid possible decomposition of ZIF-8. The HCl exposed ZIF-8/PVC (A-ZIF-8/PVC) Arrow was dried in the 200 ºC oven for 30 minutes in order to remove HCl.

A ZIF-8/PVC Arrow without HCl exposure, a pure PVC Arrow and a pure ZIF-8 Arrow were also prepared for comparison.

Before each sampling, the SPME Arrows were pre-conditioned in the GC injection port at 250 ºC for 15 minutes.

Figure 1.

2.3. Instruments and GC-MS analysis

The surface morphology of the A-ZIF-8/PVC coated SPME Arrow was studied by scanning electron microscopy (SEM) (Hitachi, model S-4800, Japan). The surface area, pore size, and pore volumes were determined by nitrogen physisorption measurements at 77 K (ASAP 2010, Micromeritics Co., Norcross, GA, USA). The X-ray photoelectron spectroscopy (XPS) spectra of the ZIF-8 coating were obtained with a PHI Quantum 2000 instrument (Physical Electronics, Inc., Chanhassen, MN, USA).

The GC-MS analysis was carried out using an Agilent 6890 N gas chromatograph coupled with an Agilent 5973 C mass selective detector or with an Agilent 5975 C mass selective detector (Agilent Technologies, Palo Alto, USA). The former mass selective detector was mainly used in coating preparation optimization and the latter one in SPME conditions optimization, method validation, and natural sample analysis. An InertCap for Amines capillary column (30 m length × 0.25 mm i.d., GL Sciences, Tokyo, Japan) was used for the chromatographic separation. The instrumental conditions of GC-MS for analysis of amines were as follows: injector temperature, 270 ºC; transfer line temperature, 250 ºC; ion source temperature, 230 ºC; quadrupole temperature, 150 ºC; oven temperature program: 40 ºC (held for 5 minutes) and then increased to 250 ºC at a rate of 30 ºC min^{-1} (held for 4 minutes). The mass spectrometer was operated in the electron ionization (EI) mode (70 eV). Data acquisition was carried out in scan mode in m/z range of 30-300. Helium (99.996% purity, AGA, Espoo, Finland) was used as carrier gas at a constant flow rate of 1.2 mL min^{-1}.

Uncoated solid phase microextraction Arrows (for coating length of 20 mm), PDMS/Carboxen-1000 Arrows (sorbent film thickness 120 μm and the sorbent length 20 mm) and PAL RTC auto-sampler were kindly provided by CTC Analytics AG (Zwingen, Switzerland).

2.4. SPME procedures

The preliminary optimization of coating preparation and SPME sampling conditions with A-ZIF-8/PVC coated Arrow analysis was carried out manually. The final optimization was performed using the CTC autosampler. The general SPME procedure was as follows: diluted amine standard solution, a stir bar (10 mm × 3 mm) and solid NaCl were added into a 20 mL headspace vial equipped with a PTFE/silicone septum screw-cap (both from Phenomenex, Torrance, California, USA). 500 µL KOH solution was then injected into the headspace vial by a 500 µL syringe in order to release the amines into the headspace. The extraction was done by puncturing the septum with the SPME Arrow and exposing the sorbent to headspace inside the vial.

The sample solution preparation and desorption procedures of automated sampling were the same to that of manual sampling given above. The difference of automatic sampling was the incubation temperature, which was 40 ºC (5 min). The extraction was carried out at 40 ºC, which was the minimum value for the sampler system.

PDMS/Carboxen-1000 Arrow was selected for the comparison with A-ZIF-8/PVC coated Arrow because of its higher extraction capacity for amines compared to other commercial SPME Arrows and SPME fibers. The optimal SPME conditions were the same as described in our previous study with small modifications.[8] For extraction, 5 mL sample solution, 2 g NaCl and 250 µL 5 M KOH were mixed, and then incubated for 10 min at room temperature. For desorption, 40 seconds at 250 ºC was used. Extraction times were optimized due to the use of an autosampler. Extraction was carried out at 40 °C.

The pre-condition time between the extractions was 10 min for both A-ZIF-8/PVC coated Arrow and commercial PDMS/Carboxen-1000 Arrow.

2.5. Natural sample applications

2.5.1. Wastewater sample analysis

178 Influent and effluent wastewater samples were from Viikinmäki municipal wastewater treatment
179 plant (WWTP), which is located in Helsinki, Finland. The samples were collected into pre-cleaned
180 plastic bottles and stored in the refrigerator at 4 ºC prior to analysis. To assess recovery with A-ZIF-
181 8/PVC SPME Arrow, influent wastewater samples (7.5 mL) were spiked with 75 and 150 µL of TMA
182 and TEA standard solution (10 mg L^{-1}), respectively. For PDMS/Carboxen-1000 SPME Arrow
183 recovery, influent samples (5.0 mL) were spiked with 50 and 100 µL of TMA and TEA standard
184 solution (10 mg L^{-1}), respectively. The spiking resulted in 100 ng mL^{-1} (TMA) and 200 ng mL^{-1} (TEA)
185 with both sample volumes.

186 **2.5.2. Fish sample analysis**

187 The salmon sample was purchased from a local supermarket in Helsinki, Finland. The sample was
188 stored at room temperature for 0, 1, 2, 3 and 4 days in order to monitor changes in the amine
189 concentrations. On the first day (day 0), the fish sample was analyzed immediately without storage.
190 The sample preparation was performed as follows: 50 mL 0.4 M $HClO_4$ was added to approximately
191 10 g of fish and the mixture was homogenized in a 1000 mL plastic graduated cylinder (Bosch,
192 Gerlingen, Germany) with a kitchen blender at maximum power for 5 minutes. The homogenate was
193 transferred into a 100 mL volumetric flask and the plastic graduated cylinder was washed with 10 mL
194 of $HClO_4$ three times and washing solutions were added into the flask. Finally, the volume of the
195 mixture was then adjusted to 100 mL with 0.4 M $HClO_4$.

196 **2.5.3. Mushroom sample analysis**

197 Four types of fruiting bodies (wood-decay fungus, Supplement Figure S1) were collected from a
198 forest near Kumpula Campus of the University of Helsinki (Helsinki, Finland) on the 1st of
199 September, 2016 and stored overnight at +4 °C. The following day they were cut into cubes with
200 diameters of roughly 1 cm. Approximately 4 grams of each sample was weighed into 50 mL Falcon
201 tube and 15 mL of 10% (w/v) TCA was added. Samples were homogenized with an IKA Ultra Turrax

202 homogenizer for 2 minutes at maximum speed and centrifuged. The supernatant was moved to a 50
203 mL volumetric flask, followed by a second homogenization of the fish in 15 mL of 10% (w/v) TCA
204 and centrifugation. The supernatant was combined with the previous one and the volume of the extract
205 was adjusted to 50 mL with 10% (w/v) TCA.

206 **3. Results and discussion.**

207 **3.1. Acidification of ZIF-8 coated SPME Arrow**

208 An SPME Arrow coated only with ZIF-8 was first prepared in order to investigate its extraction
209 efficiency towards TMA. ZIF-8 exhibited considerably lower extraction efficiencies than
210 PDMS/Carboxen-1000 Arrow as shown in Figure 2a, most probably due to the pore size of ZIF-8
211 (5.6 Å), which is smaller than the molecular size of TMA (approximately 8.4 Å)[28, 29]. This
212 prevents effective capture of the TMA molecule to the sorbent.

213 **Figure 2.**

214 ZIF-8 is sensitive to acid and its pore size can be enlarged [30]. ZIF-8 particles decompose very
215 quickly if immersed into an acid solution directly. Thus, in order to minimize the degradation, we
216 exposed ZIF-8 to a 1 M water solution of HCl in the headspace. The elemental compositions of the
217 ZIF-8 particle coatings were compared by XPS before and after the acid exposure (data not shown).
218 The composition of ZIF-8 particle appeared to be unchanged. Moreover, the pore size of ZIF-8
219 particles before and after acidification was characterized by nitrogen physisorption measurements.
220 The results indicated that before acidification the pore size of ZIF-8 particles matched the results
221 reported in the literature[29], but after the acidification, the pore size increased to about 50 nm. The
222 results from XPS and nitrogen sorption characterizations proved that headspace acidification strategy
223 was capable of changing the pore size of ZIF-8 particles without changing its elemental composition.

224 As shown in Figure 2a, the extraction performance of the acid exposed ZIF-8 coated Arrow
225 increased 1290 % in peak area compared to the non-exposed ZIF-8 Arrow, but it was still lower than

that of PDMS/Carboxen-1000 Arrow. Moreover, the stability of the ZIF-8 coating on the surface of the Arrow was poor and it was visibly damaged after only five extraction/desorption cycles. Accordingly an adhesive was needed for the preparation of a stable SPME Arrow coating. PVC was selected because it is a relatively heat-resistant polymer which can be easily dissolved in THF and reassembled after THF removal. The acid exposed ZIF-8/PVC Arrow and non-exposed ZIF-8/PVC Arrow were compared for the extraction of TMA. Due to the increased thickness of ZIF-8 (from around 5 μm to 70 μm), both Arrows showed increased extraction capacity. The increase in extraction performance after acid exposure was similar to non-PVC Arrow, 1049%. A PVC coated SPME Arrow (PVC-SPME Arrow) was prepared and tested under the same extraction and desorption conditions as ZIF-8/PVC SPME Arrow, and it did not show any extraction capability towards TMA (data not shown). Thus, it could be concluded that the extraction of TMA was caused by the acidified-ZIF-8 sorbent. By comparing acidified-ZIF-8/PVC SPME Arrow with PDMS/Carboxen-1000 SPME Arrow in Figures 2a and 2b, the extraction performance of former Arrow was 331% greater than the latter Arrow even though the coating thickness was lower (70 μm for A-ZIF-8/PVC Arrow and 120 μm for PDMS/Carboxen-1000).

3.2. Optimization of ZIF-8 coating preparation procedure

It was important to optimize the preparation of the SPME Arrow coating for the best performance. Several parameters including adhesive to sorbent ratio, number of dipping cycles, and an aging temperature were optimized. The adhesive to sorbent ratio influences the extraction performance by the amount of sorbent that has been immobilized on the Arrow surface. Four A-ZIF-8/PVC Arrows were prepared in different ZIF-8 to PVC mass ratios: 4:1, 6:1, 8:1 and 10:1. All of them were prepared in 2 mL tubes with 1 mL THF so that 20 mm long Arrow carrier could be dipped in preparation solution thoroughly. Ratios lower than 4:1 were not tested because the suspension did not have enough viscosity to stick to the stainless steel surface. On the other hand, higher than 10:1 suspension was too viscose and made it difficult to produce uniform coating along the Arrow. According to the

results shown in Figure 3a, A-ZIF-8/PVC Arrow prepared with 6:1 ratio of ZIF-8 to PVC provided the highest extraction efficiency to TMA and TEA, and this ratio was used to produce the sorbents.

The number of dipping cycles was optimized to provide a maximum thickness of A-ZIF-8/PVC coating, as higher sorbent volume results in higher extraction capacity to analytes [8] and can also improve the coating physical stability[31]. The effect of the number of dipping cycles from 1 to 7 was investigated. Over 7 cycles were not tested because the coating became too thick and could not be withdrawn inside the protective outer tube of the Arrow. As seen from Figure 3b, the extraction efficiency of amines by A-ZIF-8/PVC Arrow increased from 1 to 5 cycles. From the SEM images (Figure S2) it was observed that the thickness of A-ZIF-8/PVC coating increased from around 5 μm to 70 μm (from 1 cycle to 5 cycles). After 5 dipping cycles, the extraction efficiency increased only slightly. Thus, 5 dipping cycles were considered optimal.

Figure 3.

To select the optimal aging temperature, both the effect of temperature on the stability of the coating and minimized leaching impurities from A-ZIF-8/PVC coating during the desorption process were studied. The tested aging temperatures were 200, 220, 240, 250 and 260 ºC in the GC injection port with constant helium gas flow (1.2 mL min^{-1}) for 1 hour. No large difference in extraction capability was noticed between different aging temperatures, although 250 ºC aging temperature demonstrated slightly better extraction performance compared to that of 260 ºC (Figure 3c). 250 ºC gave a relatively clean baseline (data not shown) and was selected as the optimal aging temperature.

3.3. The repeatability, reproducibility, physical stability and reusability of ZIF-8 coating

The repeatability of optimized A-ZIF-8/PVC Arrow was investigated. The extraction conditions were following: 5 mL 1 μg mL^{-1} TMA solution, 500 μL 5M KOH with 2 g NaCl in a 20 mL headspace vial for 20 min extraction with 1400 rpm agitation, then desorption at 250 ºC for 60 seconds. The

results showed that relative standard deviation (RSD) for 29 extractions was 10.3% proving a good repeatability of A-ZIF-8/PVC Arrow for extraction of TMA.

The reproducibility of optimally produced A-ZIF-8/PVC Arrow was also investigated. Five Arrows with the optimized preparation procedure were made in a batch. The extraction and desorption conditions were same as in the repeatability study with the exception that the extraction solution was a mixture of TMA and TEA (1 μg mL^{-1}). Triplicate measurements were made with each Arrow. Satisfactory reproducibility was achieved with 15.6% RSD for TMA and 13.3% RSD for TEA (n=5).

The physical stability of optimized A-ZIF-8/PVC Arrow was investigated by comparing the Arrow before and after conditioning at 250 ºC for 28 h. The extraction and desorption conditions were the same as in the reproducibility study. No noticeable decrease in extraction performance of A-ZIF-8/PVC Arrow was seen.

Reusability of the A-ZIF-8/PVC Arrow was evaluated with repeated extraction cycles of 5 mL 1 μg mL^{-1} mixture of TMA and TEA. The conditions were the same as in the repeatability study except for desorption which was 270 ºC for 30 seconds. The results are demonstrated in Figure 4. After 130 extraction and desorption cycles, there was no significant decrease in the extraction efficiencies of both TMA and TEA with A-ZIF-8/PVC coating. The RSD% of TMA was 9.94% and that of TEA 13.03%.

Figure 4.

3.4. Optimization of SPME Arrow conditions

The extraction time optimization for both, A-ZIF-8/PVC Arrow and PDMS/Carboxen-1000 Arrow and the sample volume optimization for A-ZIF-8/PVC Arrow were carried out with a PAL RTC auto-sampler. Because the minimum extraction temperature in the instrument was 40 ºC and higher temperatures may extract large amounts of water that would affect the peak shapes in GC [8], 40 ºC was selected for all the further extractions. The agitation speed was 750 rpm.

3.4.1. Extraction conditions

At first, the KOH concentration was optimized. The concentrations varied from 1 to 10 M and 500 µL was used for each sample. Because the peak areas of the analytes increased up to 5 M, it was selected as the optimal concentration of KOH solution (Figure S3a). The effect of NaCl concentration on the peak areas of amines was investigated in the concentration range of 0-60% (w/v). The results (Figure S3b) revealed that the extracted amine amount by A-ZIF-8/PVC Arrow significantly increased with increasing NaCl concentration until the solution became saturated. Therefore, further experiments were performed at NaCl concentration of 40%. Three sample volumes 2.5, 5.0 and 7.5 mL were tested in a 20 mL vial with 40% NaCl and 250, 500, and 750 µL 5 M KOH solution. The extraction time in this experiment was 20 min and the incubation time was 10 min at 50 ºC. According to the result shown in Figure S3c, the peak areas for both TMA and TEA increased with the sample volume. So 7.5 mL was chosen as the optimal sample volume for the further experiments. Higher sample volumes were not tested due to the chance that the sorbent may contact the liquid during agitation.

The extraction time of both A-ZIF-8/PVC and PDMS/Carboxen-1000 Arrows was investigated. The extraction time of PDMS/Carboxen-1000 was reinvestigated because the extraction temperature and agitation speed were changed compared to the previous study.[8] The extraction conditions of A-ZIF-8/PVC Arrow were based on the optimum conditions mentioned above: 7.5 mL TMA and TEA mixed standard solution in a 20 mL vial, 40% NaCl, and 750 µL 5 M KOH solution. Desorption was performed at 250 ºC for 60 seconds. The extraction and desorption conditions of PDMS/Carboxen-1000 Arrow were the same as in section 2.4. The results seen in Figure 5 indicate that the A-ZIF-8/PVC Arrow reached equilibrium at 5 min, while the PDMS/Carboxen-1000 Arrow at 15 min. The shorter extraction time achieved by A-ZIF-8/PVC Arrow was mainly due to the thinner coating thickness of A-ZIF-8/PVC Arrow (70 µm) compared to that of PDMS/Carboxen-1000 (120 µm)[2].

322 Therefore, in further experiments, the extraction times of 5 minutes were used for A-ZIF-8/PVC
323 Arrow and 15 minutes for PDMS/Carboxen-1000.

324 **3.4.2. Desorption conditions**

325 Desorption temperature was varied between 205 ºC and 270 ºC. In order to ensure complete and
326 fast desorption, 270 °C was chosen. Desorption time of 30 seconds was selected, because it was
327 enough for complete desorption of analytes.

328 **Figure 5.**

329 **3.5. Method validation**

330 The analytical performance of the A-ZIF-8/PVC Arrow and commercial PDMS/Carboxen-1000
331 Arrow were investigated under optimal conditions with the PAL auto-sampler pretreatment and GC-
332 MS analysis. The linear range, limit of quantitation (LOQ) and precision were evaluated for the
333 extraction of standard TMA and TEA solution. The calibration curves of A-ZIF-8/PVC Arrow for
334 TMA and TEA were constructed with seven data points with triplicate measurements from 1 ng mL^{-1}
335 to 200 ng mL^{-1} and 1 ng mL^{-1} to 500 ng mL^{-1}, respectively. The correlation coefficient (R^2) of TMA
336 was 0.9903 and that of TEA was 0.9921. The LOQs of TMA and TEA, calculated as three times
337 standard deviation of the lowest calibration point, were both 1 ng mL^{-1}. The linearity of the calibration
338 was assessed with analysis of residuals and the RSDs of TMA and TEA in the linear range varied
339 from 2.0 to 24.1% and from 2.6 to10.1%, respectively.

340 For PDMS/Carboxen-1000 Arrow, the calibration curves were constructed with six data points
341 from 5 ng mL^{-1} to 150 ng mL^{-1} for TMA and from 3 ng mL^{-1} to 500 ng mL^{-1} for TEA, with triplicate
342 measurements. The calibration was linear and the correlation coefficient was 0.9839 for TMA, and
343 0.9934 for TEA. The LOQs of TMA and TEA were 5 ng mL^{-1} and 3 ng mL^{-1}, respectively. The RSDs
344 of TMA and TEA in the linear range were 3.1-20.3% and 1.9-13.4%, respectively. In general, both
345 A-ZIF-8/PVC Arrow and PDMS/Carboxen-1000 Arrow performed well with a good linearity and a

346 good repeatability for TMA and TEA analysis. However, A-ZIF-8/PVC Arrow exhibited lower
347 LOQs with TMA and TEA than PDMS/Carboxen-1000 Arrow. On the other hand, after comparing
348 the results with already published ones, listed in Table 1, lower LOQs were achieved in this research.

349 A NORDTEST TR 537 procedure [32] was employed for the calculation of the expanded
350 measurement uncertainty (U) for A-ZIF-8/PVC Arrow approach. U for A-ZIF-8/PVC Arrow was
351 26% for TMA and 28% for TEA within 95% confidence limit. Compared with the results of our
352 previous work [8], lower expanded uncertainty was now obtained due to the larger extraction capacity
353 of the A-ZIF-8/PVC Arrow.

354 **Table 1**

355 **3.6. Application to wastewater, salmon and mushroom sample analysis**

356 **3.6.1. Wastewater sample**

357 The developed A-ZIF-8/PVC SPME Arrow was applied to the analysis of influent and effluent
358 wastewater samples under the optimized conditions and the results were then compared with those
359 achieved by commercial PDMS/Carboxen-1000 SPME Arrow (Table 2 and Figure 6a). Both TMA
360 and TEA were detected in influent wastewater and their concentrations were 70.9±2.8 ng mL^{-1} and
361 270.9 ng±20.1 mL^{-1} by A-ZIF-8/PVC Arrow and 60.4±12.9 ng mL^{-1} and 228.8±14.6 ng mL^{-1} by
362 PDMS/Carboxen-1000 Arrow, respectively. Only TEA could be detected in effluent wastewater and
363 its concentration was lower than in the influent wastewater which means that the WWTP purification
364 process eliminates completely TMA most probably because of its high volatility and TEA only
365 partially.

366 The influent wastewater was selected for recovery experiments with spiked concentrations because
367 of its more complex matrix. The recoveries were in the range of 91.6%-92.1% and the RSDs for the
368 three replicate sampling were 7.0%-7.4%. Higher recovery of TEA and smaller RSDs were obtained
369 by A-ZIF-8/PVC Arrow compared to those obtained by PDMS/Carboxen-1000 Arrow. This may be

due to the large pore size of acidified ZIF-8 material (about 50 nm) being more suitable for larger molecular size TEA (8.4 Å). On the other hand, the pore size of Carboxen-1000 material was smaller than 8.0 Å, being worse for TEA extraction. Furthermore, both SPME Arrows exhibited the similar recoveries to TMA due to its smaller molecular size, 5.6 Å, compared to TEA. In summary, A-ZIF-8/PVC Arrow showed better extraction capability than PDMS/Carboxen-1000 Arrow for TMA and TEA.

3.6.2. Salmon sample

A-ZIF-8/PVC SPME Arrow and commercial PDMS/Carboxen-1000 SPME Arrow were also utilized for monitoring freshness of salmon by detecting TMA and TEA concentration, which are the indicators of spoilage.[33] The changes of TMA content in salmon stored at room temperature are shown in Figure S4 and the chromatograms in Figure 6b. Only TMA could be detected in salmon samples. The initial concentration of TMA was 0.020±0.003 and 0.014±0.008 mg/100 g, as determined by A-ZIF-8/PVC Arrow and PDMS/Carboxen-1000 Arrow, respectively. After three days of storage, the TMA values largely increased up to 3.58±0.389 mg/100 g (determined by A-ZIF-8/PVC Arrow) and 2.99±0.935 mg/100 g (determined by PDMS/Carboxen-1000 Arrow). The A-ZIF-8/PVC Arrow showed similar results for the amount of extracted TMA than PDMS/Carboxen-1000 Arrow when taking standard deviations into account. In addition, A-ZIF-8/PVC Arrow gave lower standard deviation compared to PDMS/Carboxen-1000 in the complex fish sample. The values and curve of TMA content increase with storage time in salmon samples were comparable to results reported earlier [34-36] and the reason for a slightly higher concentration detected in this study may be due to the higher storage temperature used.

3.6.3. Mushroom analysis

As can be seen in Figure S5, only TMA could be detected in mushroom samples, and with the ZIF-8/PVC Arrow TMA could be detected in the all four samples (#1, #2, #3 and #4) while commercial

PDMS/Carboxen-1000 Arrow could detect TMA only in three samples (#2, #3 and #4), and the peak intensity of TMA extracted by ZIF-8/PVC Arrow was regularly higher than that extracted by PDMS/Carboxen-1000 Arrow.

Figure 6.

Table 2

Conclusions

In this study, we demonstrated the applicability of ZIF-based material as SPME Arrow sorbent for the determination of small volatile amines in different sample matrices. A simple physical adhesion approach was employed for the fabrication of hydrophobic ZIF-8 material as sorbent for SPME Arrow. The pore size of ZIF-8 adsorbent was modified by headspace acidification and then used for extraction of volatile low molecular weight alkylamines. The fabricated A-ZIF-8 SPME Arrow was highly efficient, reusable and reproducible. Its potential application as SPME Arrow adsorbent was proved by the extraction of trace level amines in wastewater, salmon and mushroom samples prior to GC/MS analysis and the results were comparable with those achieved by commercial PDMS/Carboxen-1000 SPME Arrow. A-ZIF-8/PVC Arrow provided acceptable flexibility for TMA and TEA extraction in practical applications due to larger pore size of acidified ZIF-8. In addition, ZIF-8 based Arrow-GC/MS method exhibited lower limit of detections compared with those of Carboxen-1000 based Arrow-GC-MS method. Furthermore, ZIF-8-coated SPME Arrow showed satisfactory selectivity for amines in complex mixtures. Considering the porosity and modifiable structure, good physicochemical properties and large surface area, the ZIF-based MOF material is promising as adsorbent for SPME Arrow for the extraction of short chain aliphatic amines.

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538 **Figure captions**

539 Figure 1. Schematic of the fabrication of Acidified-ZIF-8/PVC SPME Arrow.

540 Figure 2. Extraction performance for trimethylamine, (a) pure ZIF-8 Arrow, acidified pure ZIF-8
541 Arrow and PDMS/Carboxen-1000 Arrow, (b) ZIF-8/PVC Arrow and acidified–ZIF-8/PVC Arrow. 5
542 mL of 1 μg mL^{-1} TMA solution for 20 minutes extraction, and desorption at 250 ºC for 60 seconds.

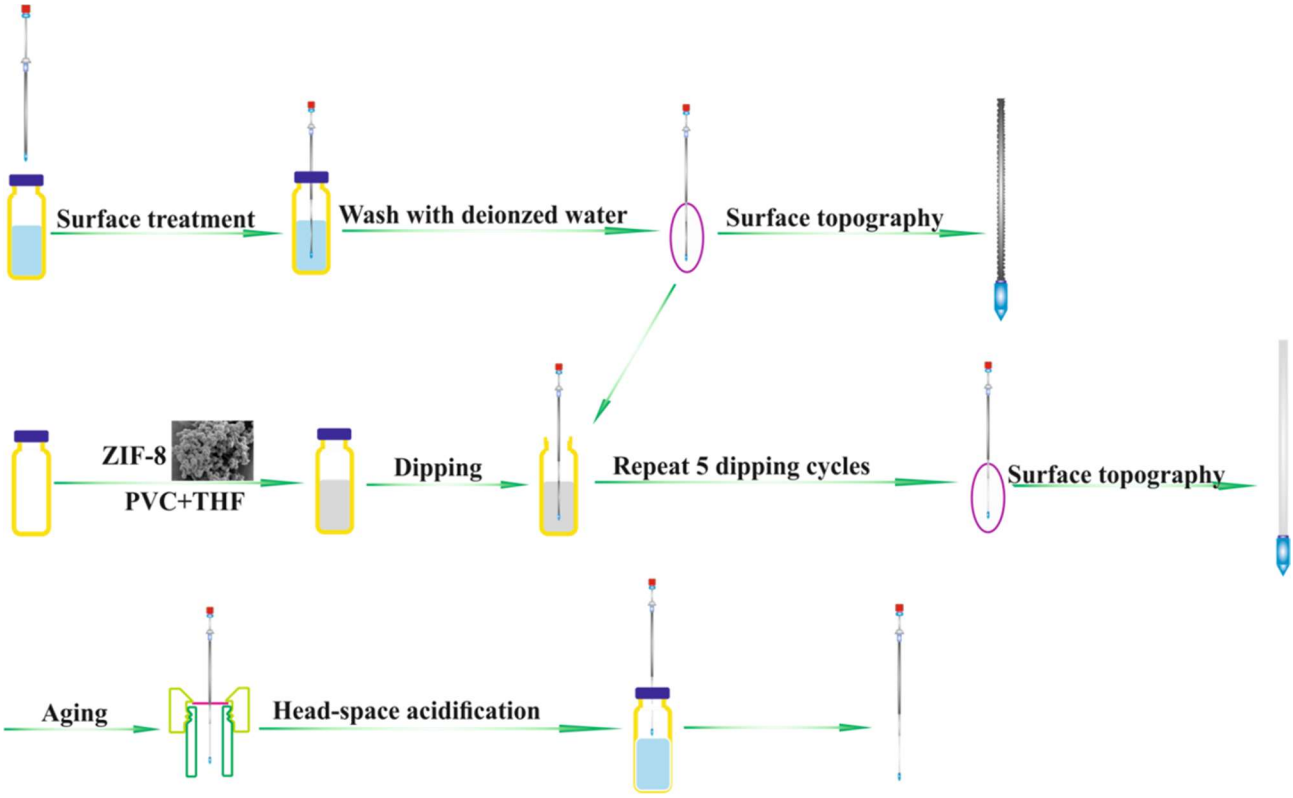
543 Figure 3. Acidified ZIF-8/PVC coating preparation optimization, (a) ZIF-8:PVC ratio optimization,
544 (b) dipping cycle optimization and (c) aging temperature optimization. 5 mL of 1 μg mL^{-1} TMA
545 solution for 20 minutes extraction and desorption at 250 ºC for 60 seconds.

546 Figure 4. Reusability of acidified-ZIF-8/PVC SPME Arrow. Relative adsorption definition: the peak
547 area of second extraction was set as 100% and the relative peak area of other extractions were
548 determined by division of the peak area by the second extraction peak area ×100.

549 Figure 5. Extraction time profiles with acidified-ZIF-8/PVC (a) and PDMS/Carboxen-1000 (b) SPME
550 Arrows.

551 Figure 6. GC-MS chromatograms of influent wastewater sample (A) and salmon sample (B) after
552 extraction with A-ZIF-8/PVC SPME Arrow (purple) and PDMS/Carboxen-1000 SPME Arrow
553 (black).

554



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557 **Figure 1.**

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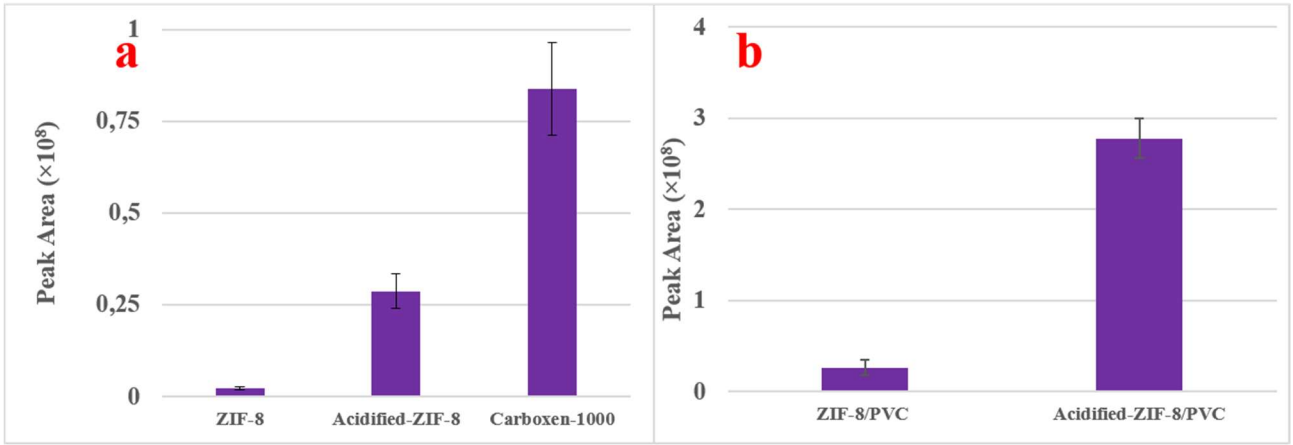

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561 **Figure 2.**

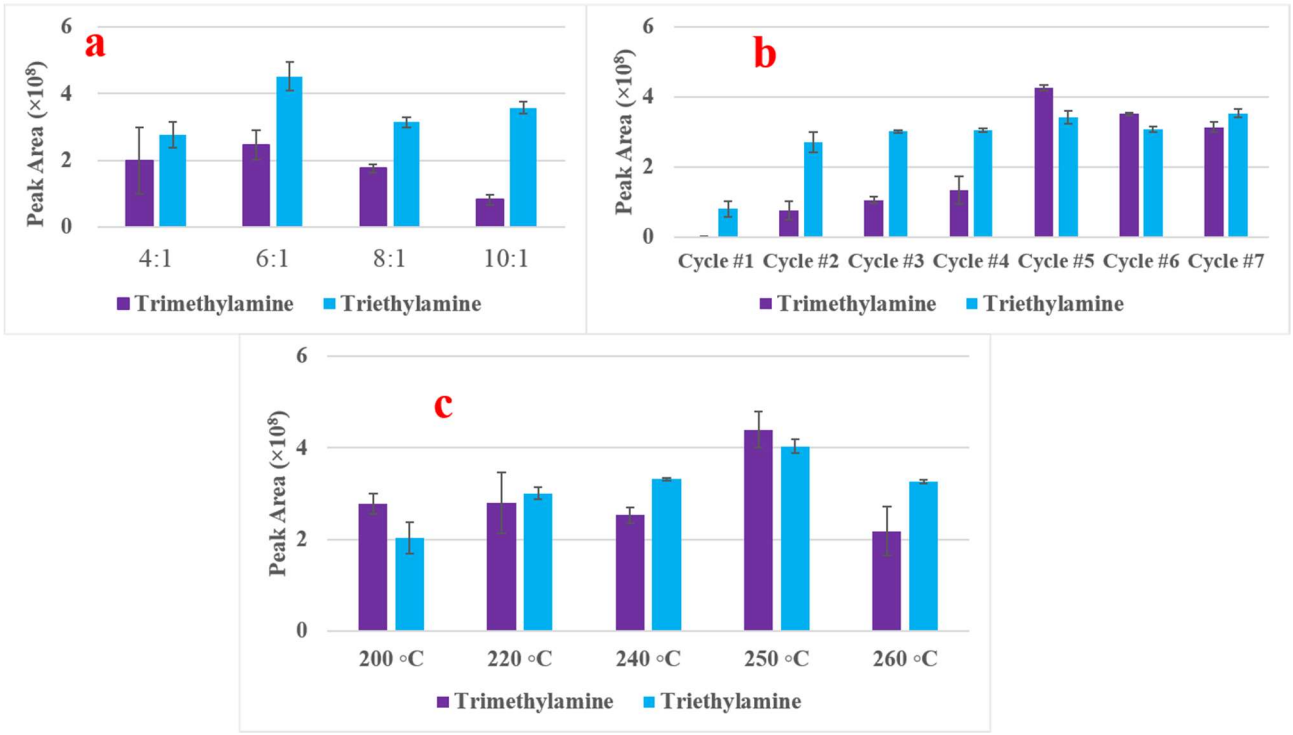
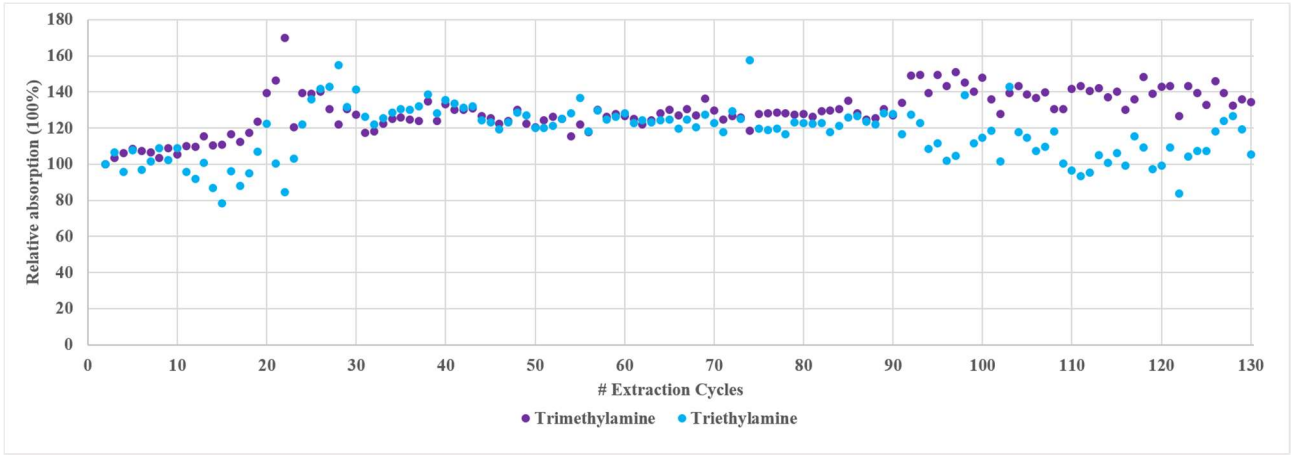


Figure 3.



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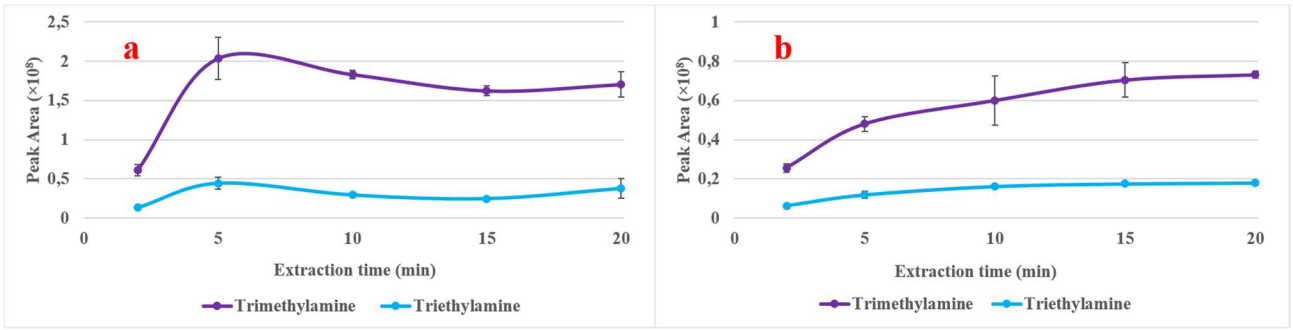

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572 **Figure 5.**

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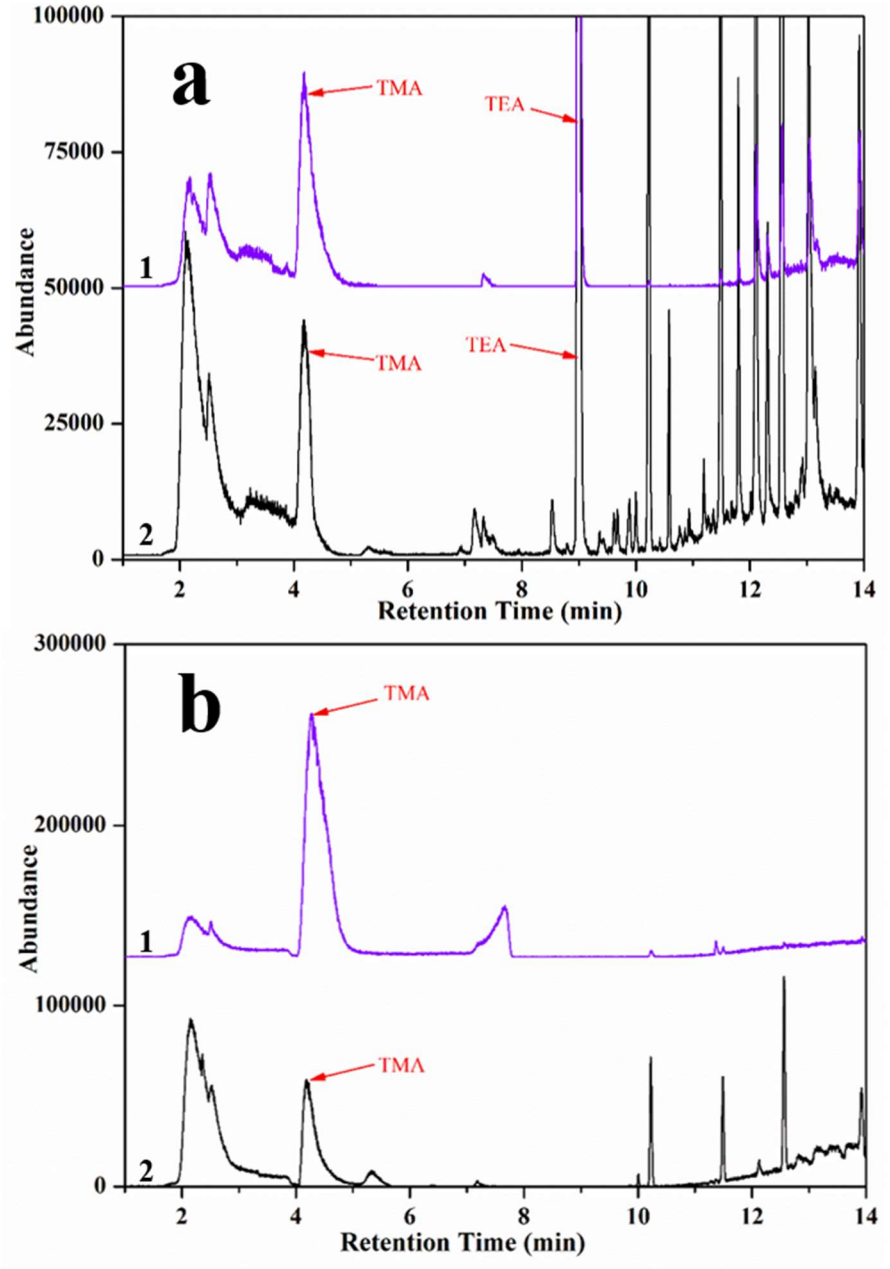

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576 **Figure 6.**

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Table 1

Comparison with other sampling methods for the determination of TMA and TEA.

Technique	Matrix	LOQ (ng mL^{-1})	Linear range (ng mL^{-1})	RSD(%)	Reference
Carboxen/PDMS-SPME-GC-MS	Gas standard	2.38 ppbv (MDL[a],TMA)	~3.2-210 ppbv (TMA)	Not provided	[15]
PDMS-SPME-GC-NPD	Wastewater and Sewage-Polluted Water	11 (LOD[b], TMA) 14 (LOD, TEA)	47-563 (TMA) 60-714 (TEA)	16 (TMA) 14 (TEA)	[37]
PDMS/DVB-SPME–GC–FID	Air	0.55 mg m^3 (TMA) 0.86 mg m^3 (TEA)	Not provided	Not provided	[38]
Amide bridged-C-SPME-GC-FID	Fish tissue	25.89 (LOD, TMA) 7.37 (LOD, TEA)	500-80000 (TMA) 50-5000 (TEA)	5.1 (TMA) 1.4 (TEA)	[39]
PDMS/DVB-SPME–GC–MS	Vegetables	58 (TMA)	Not provided	9.2 (TMA)	[40]
Carboxen/PDMS-SPME-GC-MS	Urine	14.9 µmol L^{-1} (TMA)	14.9-956 µmol L^{-1} (TMA)	12.2 (TMA)	[41]
PDMS-SPME-GC-FID	Standard TMA	0.04-0.8 mg (TMA)	2980 ng (MDL, TMA)	10 (TMA)	[42]
This article	Wasterwater Salmon Mushroom	1 (TMA) 1 (TEA)	1-200 (TMA) 1-500 (TEA)	2.0-24.1 (TMA) 2.6-10.1 (TEA)	

[a] Method detection of limit.

[b] Limit of detection

Table 2

Comparison of A-ZIF-8-SPME Arrow and PDMS/Carboxen-1000 SPME Arrow for the extraction and GC-MS analysis of wastewater.

Analytes	A-ZIF-8 SPME Arrow				PDMS/Carboxen-1000 SPME Arrow			
	Concentration (ng mL^{-1})[a]		Recovery (%)	RSD (%)	Concentration (ng mL^{-1})[a]		Recovery (%)	RSD (%)
	Effluent wastewater	Influent wastewater	Influent wastewater[b]		Effluent wastewater	Influent wastewater	Influent wastewater[b]	
Trimethylamine	Not detected	68.4±5.3	92.1	7.0	Not detected	62.2±7.8	91.6	7.4
Triethylamine	70.9±2.8	270.9±20.1	91.6	7.4	60.4±12.9	228.8±14.6	73.9	14.4

[a] Wastewater sample without spiking.

[b] Spiked with 100 ng mL^{-1} trimethylamine and 200 ng mL^{-1} triethylamine.