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Use of solid-phase microextraction for the detection of acetic acid by ion-trap gas chromatography–mass spectrometry and application to indoor levels in museums

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Abstract

A simple and efficient method using solid-phase microextraction (SPME) and gas chromatography–ion trap mass spectrometry (GC–ITMS) was developed for the analysis of acetic acid in air. The choice of the SPME fibre revealed to be critical as well as the sampling and desorption time. A dilution vessel was used for calibration. The precision of the method was found to be 4.7% relative standard deviation (RSD) and the detection limit 5.7 $\mu g\,m^{-3}$. The SPME–GC–MS technique was applied to the analysis of acetic acid in museum atmospheres.

Keywords: SPME; Acetic acid; Museum; GC–MS

1. Introduction

Volatile organic compounds (VOCs) represent a major fraction of indoor and outdoor air pollution. Even low concentrations cause malodorous atmospheres and lead to significant health hazards. Less known is their role in the deterioration of art objects which makes VOCs a threat to our cultural heritage. In particular, the emission of carboxylic acids by materials used for museum display cases has been observed [1,2]. Wood products, coatings, silicone-based sealants and polyvinyl acetate adhesives, usually employed in the fabrication of frames or storage containers, emit aldehydes and organic acids that are potentially harmful to the art objects [3]. The emission of formic, acetic, propionic, butyric and *iso*-butyric acids as well as formaldehyde has been described before [2,4]. Of special concern is the acetic acid because it leads to corrosion of metals like lead and bronze, efflorescence on calcareous materials such as mollusc shells, limestone artefacts and terra cotta, and loss of fibre strength in manuscripts.

The most suitable technique for the analysis of gaseous organic pollutants at very low levels is gas chromatography (GC). Prior isolation and enrichment procedures must bring the trace amounts of the target analytes to a concentration determinable with adequate accuracy and precision. Conventional air sampling methods comprise passive procedures via diffusion tubes or canisters, and active techniques—such as collection on filters, sorbent columns or cryogenic trapping. However, these methods are typically time-consuming and laborious, have multi-step procedures subjected to loss of analytes, and require the use of toxic organic solvents.

An innovation in sample preparation for trace analysis is the solid-phase microextraction (SPME) method, first reported by Arthur and Pawliszyn [5]. Basically SPME uses a coated fibre incorporated into a modified microsyringe. The sampling by simple exposure of the fibre to the solution or atmosphere to be studied is considered to be complete when the analyte concentration has reached an equilibrium distribution between the fibre coating and the sampled solution or air [6]. In this way, a direct proportional relationship between the sample concentration and the amount of analyte extracted is achieved. Hence, SPME combines sampling and preconcentration of the analytes into one step. The direct transfer of analytes by thermal desorption into the heated injection port

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of a GC ensure efficient use of the sample, whereas the selective nature of coatings eliminates the need of cleanup steps. A complete description about the theory and use of SPME has been reported in several reviews [6–9].

Simplicity and easy of operation make SPME a valuable alternative to more established techniques in many applications. However, as SPME analysis is based on equilibrium, calibration is a challenging task. The main difficulty exists in generating standard atmospheres to check the performances of the SPME fibres under conditions that are representative of the studied sampling environment. In the case of museum atmospheres, air circulation is often minimized to reduce outdoor contamination and low air exchange conditions exist [10]. Therefore, chamber methods are the most adequate to study concentrations of pollutants emitted from materials in enclosures and/or internal ventilation effects, since for gaseous samples natural convection of air is enough to facilitate a fast equilibration between sample and fibre [7].

This paper presents the development of a SPME–GC–mass spectrometry (MS) method for the determination of acetic acid in museum atmospheres as well as environments with low air fluxes (atmospheric, indoor and workplace air). A static method is proposed to calibrate the SPME sampling of acetic acid vapour levels present in the gaseous mixtures. Factors affecting the analysis such as fibre coating, sampling and desorption time have been studied, and analytical parameters such as linearity, repeatability and detection limit are determined. The optimized method has been applied to the analysis of samples collected at The Rubens House Museum in Antwerp, Belgium.

2. Experimental

2.1. Gaseous standard preparation

A static calibration was achieved using a gas sampling vessel (1 L, Supelco, Belgium) with acetic acid vapours in air between 10 and 500 $\mu g\,m^{-3}$. The desired concentrations were obtained by injecting different amounts of saturated acetic acid vapour into the vessel through a half-hole septum by means of a gas tight syringe (Hamilton Series 1700). Saturated acetic acid vapours were taken from the headspace above glacial acetic acid (Merck 100%, Suprapur) in a 10 mL vial sealed with a Teflon® septum. After spiking, the vessel was shacked for 60 s and then equilibrated at room temperature for 30 min. To load the SPME fibre, the septum of the calibration vessel was pierced with the SPME syringe needle, the fibre was pushed out from the needle and exposed to a standard mixture for a given time and then, withdrawn into the needle, immediately introduced into the GC injector.

Calibration working standards were prepared fresh daily from lower to higher amounts to generate progressive concentrations of acetic acid in the gas phase. The vessel was silanized once every 6 months to deactivate their interior surfaces. It was flushed with nitrogen (Air Liquid, Liége, Belgium) at room temperature for 1 h prior to use in order to remove trace contaminants. All standard concentration measurements were performed in triplicate at room temperature ($21 \pm 2\,^{\circ}C$).

The amount of headspace used to generate a given acid concentration inside the vessel was calculated according to the method of Ryhl-Svendsen and Glastrup [10].

2.2. Apparatus and instrument parameters

A manual SPME holder (Supelco, Belgium) was used for sampling. Following fibre coatings (Supelco, Belgium) were tested: 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 65 μm Carbowax®/divinylbenzene (CW/DVB), and 75 μm Carboxen™/polydimethylsiloxane (CAR/PDMS). The fibres were conditioned according to the manufacturer recommendations. Fibre blanks were run to ensure removal of contaminants before exposure to the air sample. Blanks were also run between each sample and fibre was reconditioned in case contaminants were detected. Sampling time (up to 60 min), desorption time (1–5 min), and desorption temperature (250–300 °C) were studied for the fibre coating with the best recovery and a calibration curve was constructed.

A Varian 3800 GC (Walnut Creek, CA, USA) instrument equipped with a CPWAX 52 capillary column (25 m × 0.32 mm i.d.; $d_f = 1.2$ μm, Varian-Chrompack) and a split/splitless injection port was used for GC analysis. In order to allow high desorption temperatures to be used, a guard column of deactivated fused silica (50 cm × 0.32 mm i.d.) was employed since the maximum allowable oven temperature (MAOT) for the polyethylene glycol (WAX) column is 250 °C. The split/splitless injection port was equipped with a 0.8 mm i.d. liner with the purge valve closed for 120 s. The oven temperature was programmed as follows: 60 °C for 1 min, then ramped at $25\,^{\circ}C\,min^{-1}$ to 200 °C and held for 0.9 min. Helium (Air Liquide) was used as carrier gas.

A Varian Saturn 2000 ion trap MS was used as detection system. Transferline and trap temperatures were optimized in 190 and 200 °C, respectively. The mass spectrometer was operated in the EI mode and turned off the first 180 s of the run to prevent overloading of the trap and detector. The mass range scanned was from 10 to 300 amu and the scan rate was $0.29\,s\,scan^{-1}$.

3. Results and discussion

3.1. Fibre coating

The sensitivity and selectivity of four different fibre coatings in the extraction of acetic acid from air samples were investigated, and the results are showed in Fig. 1. For the sake of clarity the error bars have been omitted from this and the following figures because the precision of better than 10% (RSD) is significantly smaller than the differences to

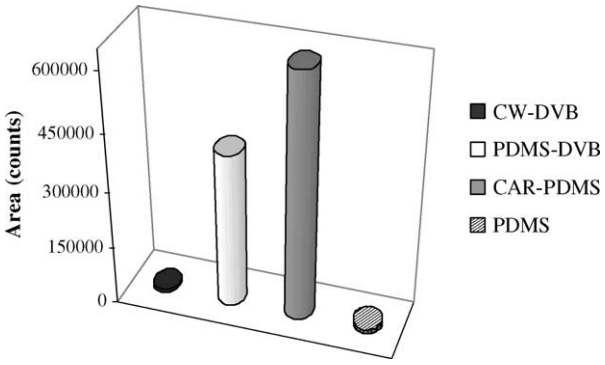

Fig. 1. Selectivity of the fibre coatings for sampling of acetic acid air standard.

be observed between different coatings or instrument settings. The 75 μm CAR/PDMS coating gives the best recovery, what is in agreement with the determination of acetic acid in another reported application [11]. Apparently the adsorption process on porous Carboxen™ particles maximizes capture of polar compounds. Furthermore, analytes can migrate between the porous layers, which increase the adsorption capacity [7]. Indeed, the adsorption of small polar molecules seems to be essentially governed by the molecular volume formed by micropores in Carboxen™ [12]. Also PDMS/DVB shows good recovery, but lower than CAR/PDMS because DVB is essentially composed of wide pores and therefore less suitable to sampling small molecules. In contrast, DVB aims at capturing aromatic molecules due to interactions with its phenyl ring and PDMS, a non-polar phase, shows bad recovery for a polar analyte. Hence, the 75 μm Carboxen™/polydimethylsiloxane (CAR/PDMS) coating has been used in all subsequent experiments.

3.2. Sampling and desorption time

The efficiency of the CAR/PDMS fibre was demonstrated by plotting peak area against adsorption time (Fig. 2). The equilibration time is defined as the time after which the amount of analyte extracted remains constant and corresponds, within the limits of experimental error (better than

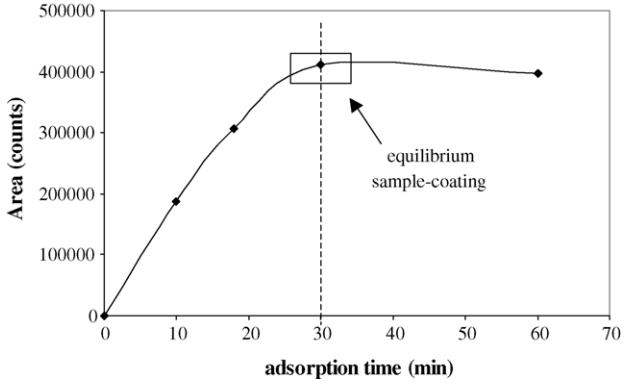

Fig. 2. Extraction time profile for acetic acid using 75 μm CAR/PDMS fibre.

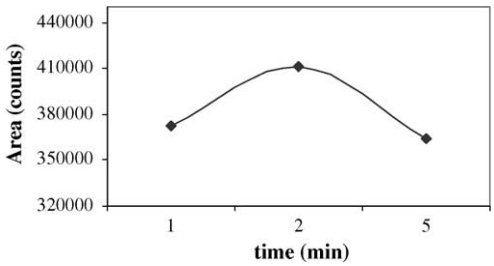

Fig. 3. Desorption time profile for acetic acid using 75 μm CAR/PDMS fibre.

10%), to the amount extracted at infinite time [13]. Experiments show that the equilibration time is 30 min, where small variations in the extraction time do not affect the amount of the analyte extracted by the fibre. Carboxen™ is a carbon molecular sieve containing mainly micropores, which cause the relatively slow mass transfer of the acetic acid through the coating. At shorter sampling times the SPME fibre is not saturated and less molecular interactions occur. All subsequent experiments have used a sampling time of 30 min.

Fig. 3 shows desorption time profile for acetic acid extracted for 30 min using CAR/PDMS fibre. No extreme difference is observed in the amount desorbed between 1 and 5 min. Further experiments have used a 2 min desorption time.

In order to verify the desorption efficiency, residual acetic acid levels were checked by a second injection for different sampling times and standard concentrations. Fig. 4 shows the results. For 30 min sampling time, the remaining acetic acid ranged from 0.4 to 2.5% for standard concentrations of 25 and 200 $\mu g\,m^{-3}$, respectively. Unexpectedly, at low concentration and short sampling time, up to 36% of the acetic acid concentration remains undesorbed after the first injection. The reason for this effect is not yet understood. However, at the optimized sampling time of 30 min or longer, only one injection is sufficient to desorb acetic acid.

3.3. Ion trap, transferline and injector temperatures

According to Fig. 5, high temperatures used for both ion trap and transferline decreased the detected signal intensities. The optimized temperatures were 200 and 190 °C for ion

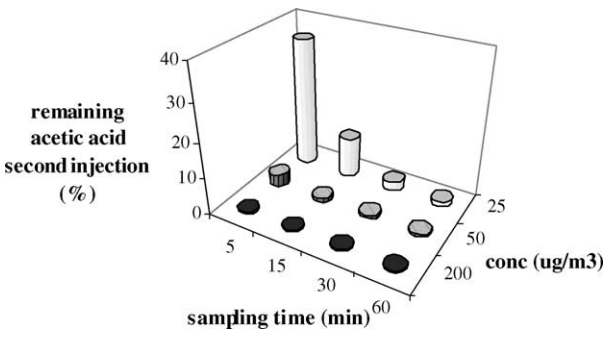

Fig. 4. Desorption efficiency of CAR/PDMS fibre for acetic acid in function of sampling time and analyte concentration.

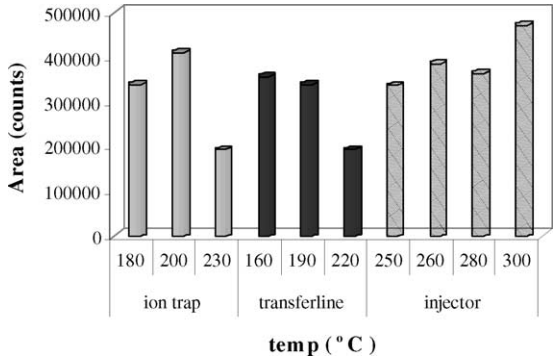

Fig. 5. Ion trap, transferline and injector temperatures optimization.

trap and transferline, respectively. Although a transferline temperature of 160 °C yielded slightly higher recovery than 190 °C, the latter value was chosen to avoid condensation since the maximum temperature for the column was 200 °C.

Fig. 6 compares the desorption efficiency as a function of the injector temperature between 250 and 300 °C. At 300 °C desorption is indeed more effective and produces lower blanks after the first injection. A guard column at the injector side was used to protect the phase at the head of the analytical capillary column and allowed the injector temperature to be set above the MAOT.

3.4. Calibration curves, limit of detection, repeatability

Fig. 7a shows the total ion chromatogram for a calibration sample taken from a calibration vessel containing 73 μg m^{-3} of acetic acid. The accompanying Fig. 7b shows a maximum for the mass chromatogram of the molecular ion from acetic acid at *m/z* 60 at 5.62 min. However, the mass spectrum (Fig. 7d) taken at a maximum of this peak still shows the presence of important signals that are not directly related to acetic acid. Specifically, all the ions from *m/z* 70 onwards are tentatively associated with the elution of PDMS-related compound. The low mass resolution capability of the ion trap prevented further elucidation of the structure. Hence, possible interferences from its fragments on the signals to be used for acetic acid must be accounted for. However, the reconstructed ion chromatogram (RIC) for mass 267 in Fig. 7c shows that careful integration of the mass chromatograms of

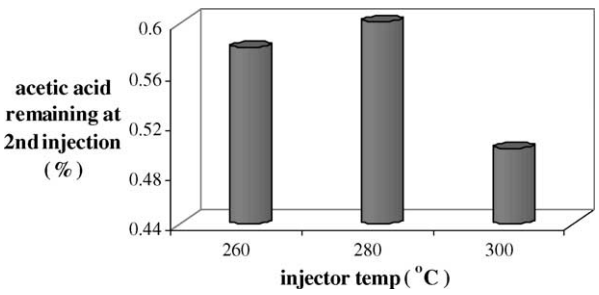

Fig. 6. Desorption efficiency of CAR/PDMS fibre in function of injector temperature.

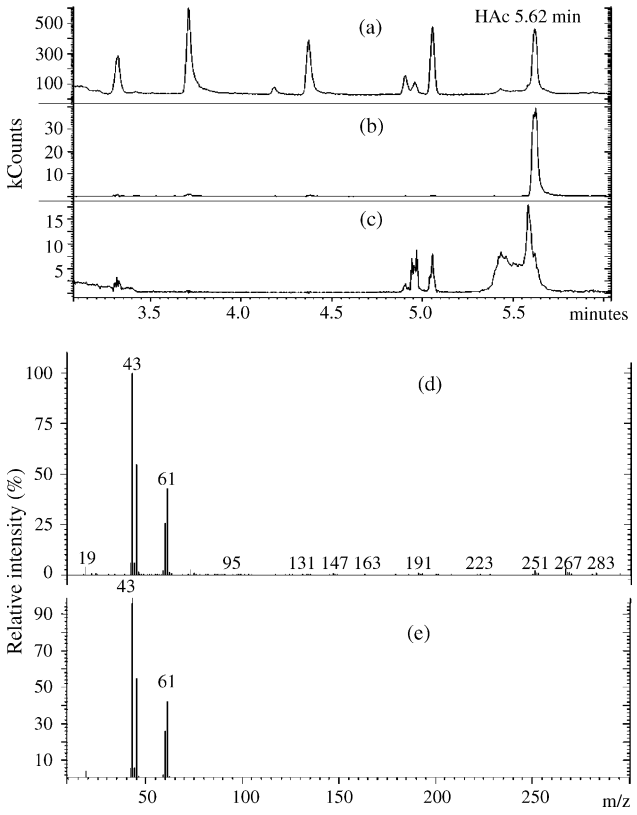

Fig. 7. Analysis of a sample taken from a calibration vessel filled with 73 μg m^{-3} acetic acid vapour standard sampled for 30 min with a CAR/PDMS fibre: (a) total ion chromatogram; (b) mass chromatogram for the molecular of acetic acid at *m/z* 60; (c) mass chromatogram for *m/z* 267; (d) mass spectrum taken at the maximum of the mass chromatogram at *m/z* 60; (e) corresponding background corrected mass spectrum.

m/z 60 should allow measure systematic errors to be eliminated. The background corrected mass spectrum given in Fig. 7e additionally supports our approach.

With respect to the ions to be used for quantifying acetic acid, molecular ions at *m/z* 60, protonated molecules at *m/z* 61 and/or acetyl fragments can be considered. In particular the use of summed intensities could be expected to improve the detection. It is well known that polar analytes undergo self-chemical ionization (self-CI) at high concentrations in ion trap. The protonated molecules as well as the molecular ions may undergo fragmentation to the common acetyl-ion. Both self-CI (function of the concentration) and fragmentation can be expected to decrease the molecular ion intensity.

Consequently the dynamic range and linearity of the calibration for the signal as a function of the acetic acid concentration in the vessel was verified for the individual peak intensities as well as for their different combinations (e.g. *m/z* 60 + 61, 60 + 61 + 43, etc.). The studied concentration range was 10.0–200 μg m^{-3} of acetic acid in air. Three independent measurements were performed at ambient temperature (21 ± 2 °C) for each concentration. The intensities of all but ions at *m/z* 60 showed a non-linear dependence on the acetic acid concentration. However, the characterization of the ion

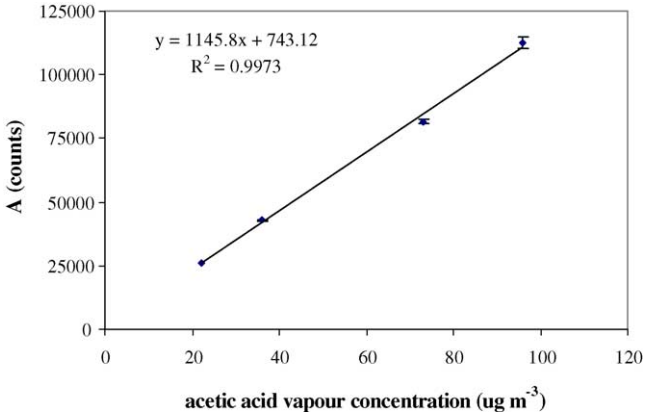

Fig. 8. Calibration curve for the molecular ion *m/z* 60 obtained via SPME–GC–MS of acetic acid in air.

at *m/z* 60 is clear and its linear range for quantification extended from 22 to 96 μg m^{-3} (see Fig. 8) with a correlation coefficient (*r*) of 0.997.

The limit of detection was estimated as three times the standard deviation obtained after six injections of the lowest concentration of the calibration curve [13]. The obtained value, 5.7 μg m^{-3} of acetic acid in air, compares to that determined by Ryhl-Svendsen and Glastrup [10] and was significantly better than that reported by Gibson et al. (44 μg m^{-3}, using a passive sampler and sampling time of 2 weeks) [14].

Repeating a standard injection 10 times, the standard deviation for the measurements was about 4.7% demonstrating the precision of the method.

3.5. Analysis of real samples

The optimized method was applied to the analysis of acetic acid in air samples collected at The Rubens House Museum in Antwerp, Belgium. Two showcases and the two respective rooms were sampled. The first showcase contained silver objects and the second one contained a chair dating from 1633, used by the famous painter Rubens. The showcases

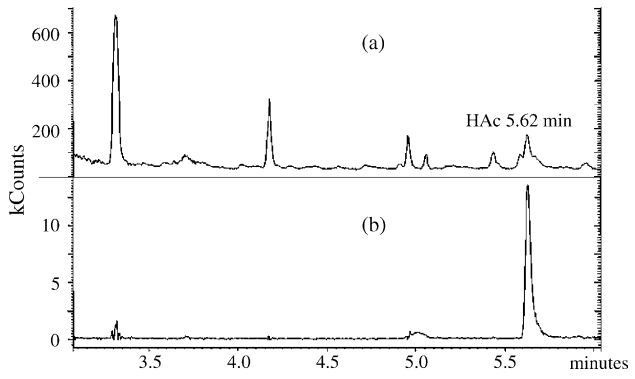

Fig. 9. Analysis of a sample taken from the atmosphere inside a silver showcase sampled for 30 min with a CAR/PDMS fibre: (a) total ion chromatogram; (b) mass chromatogram for the molecular of acetic acid at *m/z* 60.

Table 1
Acetic acid concentrations detected in air samples from The Rubens House, Antwerp, Belgium, using SPME (CAR/PDMS)–GC–MS

Place	Temperature (°C)	Acetic acid concentration (μg m^{-3})[a]
Chair showcase	21.3	98
Chair showcase room	20.5	50
Silver showcase	18.5	66
Silver showcase room	16.8	24

[a] Precision of the method = 4.7% (see text).

are sealed, preventing air exchange with outside. Samples were taken using a 75 μm CAR/PDMS SPME field sampler exposed for 30 min and analyzed by GC–MS as soon as possible. Fig. 9 shows the total ion chromatogram and the mass chromatogram at *m/z* 60 for a real sample. Scanning the mass chromatograms between *m/z* 50 and *m/z* 300 in the elution window between 5 and 6 min showed the absence of interfering compounds that would co-elute with acetic acid.

The quantitative results are presented in Table 1. As expected, a higher concentration has been observed inside the showcase with Rubens' chair, most likely due to the wood which the chair is made. Oak is well known as acetic acid emitter [10,15,16]. Such level of concentration (98 μg m^{-3}) is of great concern since the unique object of art presents some signs of deterioration. The concentration of acetic acid outside the chair showcase is 50 μg m^{-3}, i.e. about half of the value inside. This reflects the presence of a source for acetic acid inside the case. Relatively high concentrations of acetic acid have been observed inside the silver showcase, most likely originated from the construction material of its base. The concentration observed in the room is again less than half of that observed inside the case.

4. Conclusions

The method here described is versatile and convenient for the determination of acetic acid in indoor samples. It combines short analysis time with relatively low costs since no pumps, sorbents and solvents are needed. The latter is also important for the environment. The reduced sampling time combined with the reduced size of the setup is another asset when public places, such as museums, must be sampled. The analysis of acetic acid at low ppb levels in air samples is of extreme importance for museum environments. The damage to art objects caused by the presence of organic acids is irreversible. The need to monitor their atmospheric concentrations in storage and display environments is increasingly felt to be for preventive conservation in museums.

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