

# SPME–GC/MS analysis of organic acids in indoor museum environments

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## ABSTRACT

Sampling of formic and acetic acids in air on solid phase micro-extraction (SPME) has previously been suggested for polyacrylate coated SPME needles. We have tested SPME with carboxen/polydimethylsiloxane coatings, which showed to have 40 times better sensitivity for acetic acid and 4.9 times better for formic acid, than polyacrylate. The use of SPME sampling is demonstrated by the measurement of the equilibrium concentration of formic and acetic acids, which were built up by emission from a MDF board in a chamber test.

## INDEX TERMS

Acetic acid; Formic acid; Concentration measurement; SPME-GC/MS; Museum

## INTRODUCTION

Organic acids are significant when studying museum environments, since they react with the surface of objects even at very low concentrations. In contrast to human reactions to pollutants, which are often thought to require a minimum concentration level (threshold) before inducing damaging effects, the reaction with materials is often proportional to the total amount of pollutants in the air. Reactions with museum objects, therefore, depends both on the flux from pollutant emitting surfaces and on the flux reaching their target surface.

In addition, *in-situ* measurements of organic pollutants in museum environments often have to be made in confined areas such as display cases, which restricts the size of sample taken for analysis in order to minimize dilution effects from outside air. These parameters require an analytical method, which can collect a relatively small sample and still enable us to quantitate down to the lower  $\mu\text{g}/\text{m}^3$  level. We have previously demonstrated that solid phase micro-extraction (SPME) is a simple, rapid and effective method to collect formic and acetic acids in air, followed by GC/MS analysis (Ryhl-Svendsen and Glastrup, 2002). We present recent improvements to this technique in this paper.

## MATERIALS AND METHOD

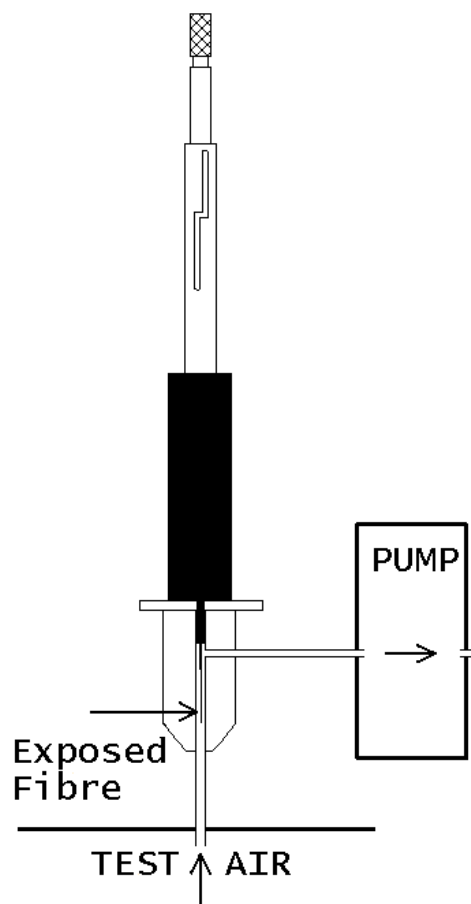
SPME consists of a fused glass fibre, coated with an adsorbent polymer. The fibre is protected inside a hollow needle on a syringe-like holder, and is only exposed for sampling and analysis. For sampling polar compounds such as formic and acetic acids, SPME fibres with a carboxen/polydimethylsiloxane coating were used. The SPME technique is described in detail by Pawliszyn (1997).

### Sampling Set-up

Sampling is performed by exposing the fibre into a stream of air, sampled from the microclimate in question. Positioned in a septum injector (Omnifit Universal Septum Injector 3301), air is dragged over the adsorbent part of the fibre at a rate of 4.11 ml/s. Sufficient exposure time is 15 min, which gives a total sample size of 3700 ml. The air sample is sucked out with a pump (SKC 222-3 Personal Air Sampler Pump), positioned after the septum injector (Figure 1).

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**Figure 1** The positioning of the SPME needle holder with the needle exposed in the universal septum injector.

### Analysis

After exposure, the fibre was transferred directly to a gas chromatograph/mass spectroscopy (GC/MS) system (Saturn 2000) where the sample was transferred to the GC column by baking the fibre. After this, the fibre was clean and could be reused for sampling.

The GC/MS method used the following conditions:

1. Injector: SPI (On-column type)
  - a. Initial temperature: 220°C.
  - b. Initial inlet pressure: 22 psi.
  - c. Column oven: initial temperature 50°C for 2 min., 20°C/min to 150°C, 30°C/min to 230°C, hold for 3 min.
2. Transfer line: 230°C.
3. Trap temperature: 190°C.
4. MS scanned from 19 to 149  $m/z$ , ion preparation SIS, with exclusion of  $m/z$  28 and 32.
5. Mass spectrometer tuned through autotune.

### Calibration

Calibration of the fibre was done by exposing it to standard concentrations of formic and acetic acids in the range of 69–400 and 86–499  $\mu\text{g}/\text{m}^3$ . These standard atmospheres were created, by passing clean air over homemade permeation tubes, made from Teflon tube (1/8" o.d. and 1/16" i.d.). The tubes were filled with formic or acetic acid and plugged in the ends with a glass rod. The active zone was approximately 10 mm. The permeation tubes were

placed inside a glass tube with an inner diameter of 6 mm, which was placed in an oven at 45°C (proportionally controlled), with pure air passing over the tubes at 10.0 ml/min. The tubes were left for 72 h before calibration. Calibration was done by removing these from the oven, allowing them to cool for 10 min. before weighing, using an analytical balance. Weighing was repeated every third day, totally 9 days, before the average evaporation from the tubes was calculated. All results are averaged on basis of three independent measurements. Diluting air was added to the gas stream at a rate of 350–2100 ml/min.

### Example of Use

An MDF board was screened for its emission of acetic and formic acids. The board was placed in a 0.227 m<sup>3</sup> steel chamber, at 23°C and 40% RH. The chamber had an internal fan, which ensured a constant mixing of the inside air. The chamber system was static, with no replacement of air during the test. Air samples was taken through a loop of metal tubes, driven by a pump (SKC 222-3 Personal Air Sampler Pump), which delivered the air back into the chamber after passing over the SPME needle. Sampling was repeated until the concentration values became stable, meaning that equilibrium was reached in the chamber.

## RESULTS

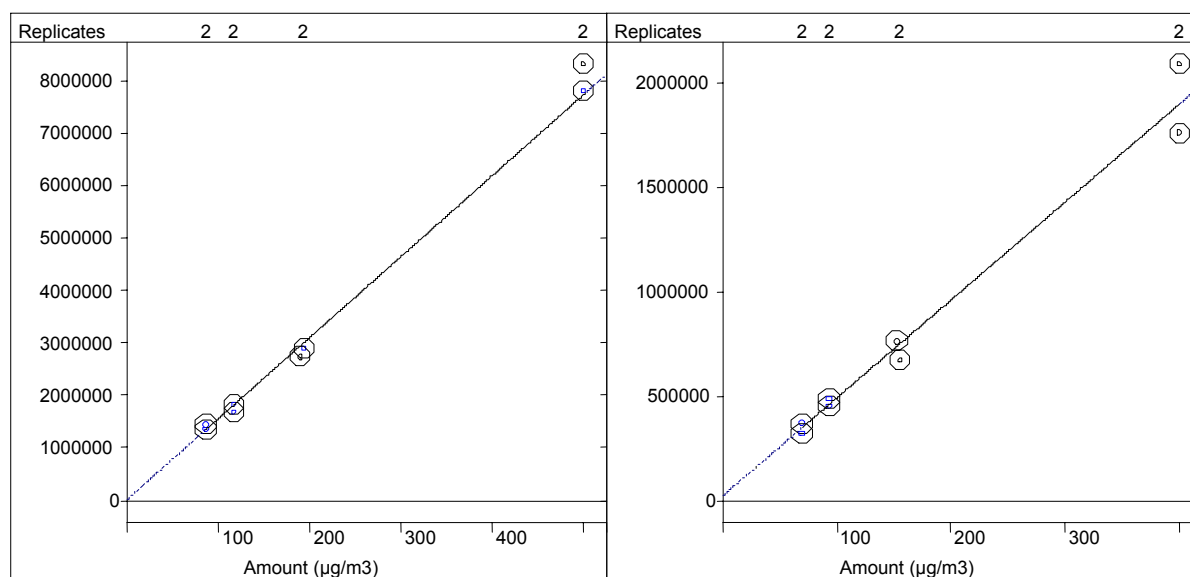
### Calibration

#### Acetic acid

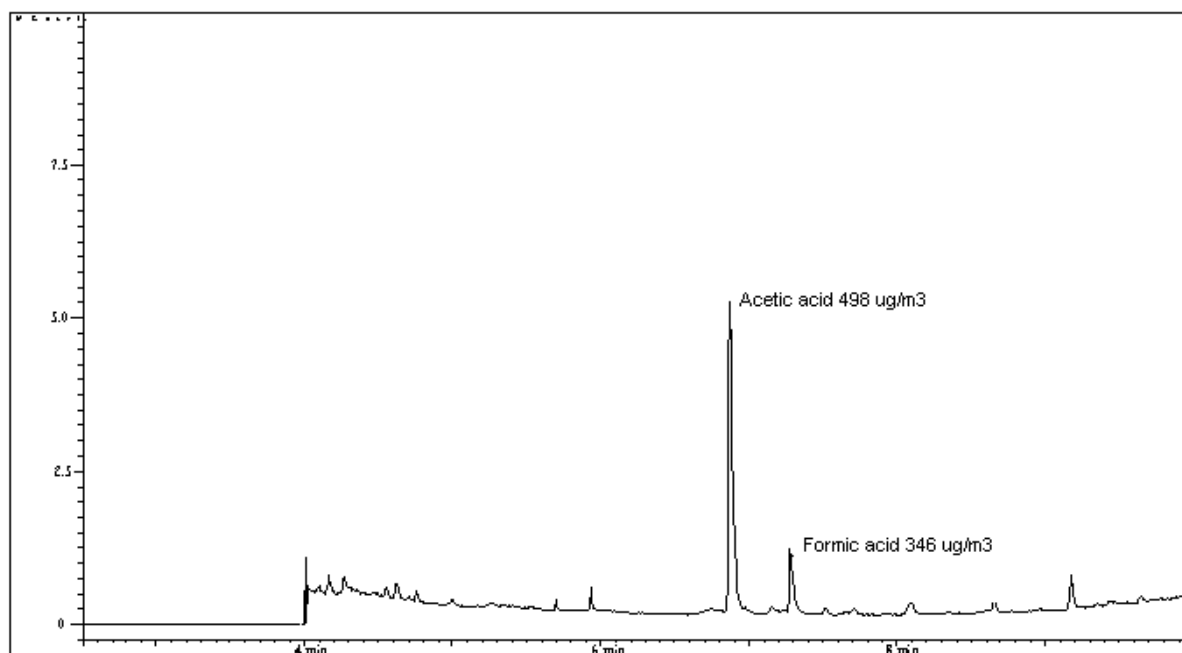
Curve Fit: Linear, Origin: Ignore, Weight: 1/nX2  
 Resp. Fact. RSD: 5,677%, Coeff. Det.(r2): 0,996  
 $y = +1,5421e+4x +2,1468e+4$

#### Formic acid

Curve Fit: Linear, Origin: Ignore, Weight: 1/nX2  
 Resp. Fact. RSD: 8,084%, Coeff. Det.(r2): 0,980  
 $y = +4673,8516x +2,3826e+4$



**Figure 2** The calibration curves for formic and acetic acids.



**Figure 3** Chromatogram of the emission from a MDF board.

Test conditions were: board surface area,  $0.3078 \text{ m}^2$ ; air exchange rate of chamber,  $0 \text{ h}^{-1}$ ; test climate,  $23 \pm 2^\circ\text{C}$  and  $40\% \text{ RH} \pm 5\%$ . The sample was taken 38 days after the insertion of the board, where the chamber concentrations had reached equilibrium.

## DISCUSSION AND CONCLUSION

In Figure 2, the calibration curves for formic and acetic acid is shown. Based on the slope, the sensitivity of this type of needle (carboxen/polydimethylsiloxane) is 40 times better for acetic acid and 4.9 times better for formic acid, than the needle used in the previous study (Ryhl-Svendsen and Glastrup, 2002), which was coated with polyacrylate. It should be mentioned, however, that the sensitivity of the needles depends on age, batch number and possible chipping off the tip of the needle. Regular calibration is, therefore, necessary.

An example of the practical use of this sampling method is the measurement of the equilibrium concentrations of organic acids at the test of the MDF board in a climate chamber. Similar to a museum display case, the test chamber was a static, airtight system, where the inserted MDF board emitted acid vapours to the inside air, as it happens in a case made from wood products. In the chromatogram shown in Figure 3, peaks for formic and acetic acids are marked, concentrations were  $346 \mu\text{g}/\text{m}^3$  for formic acid and  $498 \mu\text{g}/\text{m}^3$  for acetic acid. Construction materials, which produce such amounts of organic acids, should always be avoided in the proximity of susceptible museum objects, because of the danger of corrosion and other deterioration processes (see, e.g. Ryhl-Svendsen, 2003).

The use of SPME has a large potential for sampling the organic air pollutants, which are of a special concern in the museum environment, be it for laboratory testing, or *in-situ* investigations.

## ACKNOWLEDGEMENTS

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