



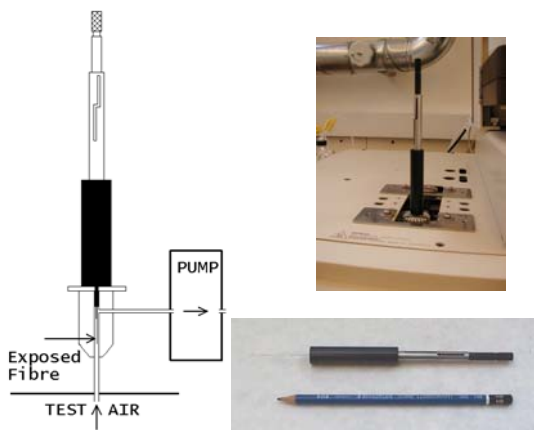
SPME-GC/MS ANALYSIS OF FORMIC AND ACETIC ACID IN AIR – RECENT IMPROVEMENTS

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Introduction

For air analysis, solid phase microextraction (SPME) is useful as 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 SPME is a simple, rapid and effective method to collect formic and acetic acid in air, followed by GC/MS analysis. The detection limits were 28.9 and 5.3 $\mu\text{g}/\text{m}^3$ respectively (Ryhl-Svendsen and Glastrup, 2002).



What is SPME?

A fused glass fibre, coated with an adsorbent polymer.

Protected inside a hollow needle on a syringe-like holder, the fibre is only exposed during sampling and analysis.

After exposure, the fibre can be transferred directly to a chromatographic system (eg. GC/MS) where the sample is transferred to the GC column by baking the fibre. After this, the fibre can be reused for sampling.

Technique

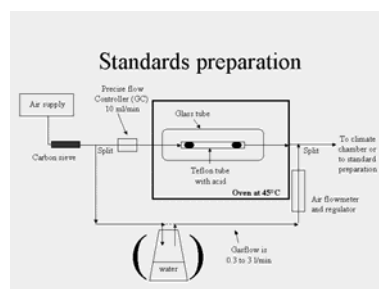
Sampling set-up

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 minutes, total sample size is 3700 mL.

Calibration

Fibre was exposed to standard concentrations of formic and acetic acids in the range of 69-400 and 86-499 $\mu\text{g}/\text{m}^3$.



Standard atmospheres were created, by passing clean air over homemade Teflon permeation tubes at 45°C, with formic and acetic acid.



Calibration was done by weighing the tubes after 72 h, repeated every third day, all in all for 9 days. From this the average evaporation rate from the tubes was calculated, and the concentration of the acids in the air stream could be calculated.

Fibres were analysed on a gas chromatograph/mass spectroscopy system (Saturn 2000)

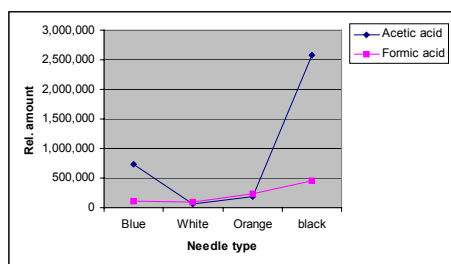


Results

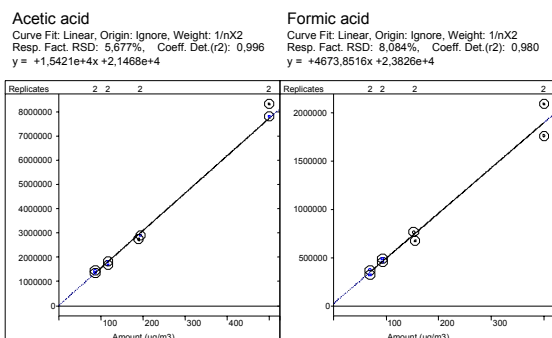
Choice of fiber

We have tested SPME fibers with different phases, all were exposed to mixed standards of 200 µg/m³ of formic acid and 200 µg/m³ acetic acid:

- Polydimethylsiloxane/divinylbenzene (blue)
- Carbowax/divinylbenzene (orange),
- Carboxen/polydimethylsiloxane (black)
- Polyacrylate (white)



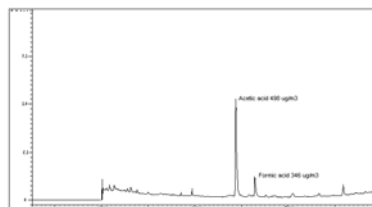
Carboxen/polydimethylsiloxane was chosen as the most sensitive fibre



Above the calibration curves for formic and acetic acid is shown. Based on the slope, the sensitivity of carboxen/polydimethylsiloxane is 40 times better for acetic acid and 4.9 times better for formic acid, than the polyacrylate fibre used in the previous study (Ryhl-Svendsen and Glastrup, 2002)

It should be mentioned, however, that the sensitivity of the needles is depending on age, batch number and possible chipping off the tip of the needle. Regular calibration is therefore necessary.

Example of use



Chromatogram of the emission from a MDF board.

Test conditions were:

- Board surface area: 0.3078 m²
- Air exchange rate of chamber: 0 h⁻¹
- Chamber volume: 0.227 m³
- Test climate: 23 °C ± 2 °C and 40% RH ± 5%.

The sample was taken after 38 days after the insertion of the board, where the chamber concentrations had reached equilibrium.

The use of SPME for 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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Reference

Ryhl-Svendsen & Glastrup, 2002. Acetic acid and formic acid concentrations in the museum environment measured by SPME-GC/MS, *Atmospheric Environment*, 36, 3909–3916.

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