## Determination of formic and acetic acid emissions in indoor air or from building products

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### Abstract

Several construction and building materials, including wood, glue and coatings, are possible sources of very volatile organic compounds (VOCs) and volatile organic compounds (VOCs) like formic and acetic acid. Due to very high air tightness and very low air exchange rates in new buildings concentrations of these harmful substances can increase considerably. To minimize the risk, emissions from building products should be identified and quantified. The common standard method, this means Tenax® sampling followed by thermal desorption and GC-MS analysis, these acids could not be detected sufficiently. The aim of this study is the comparison of two different methods for the determination of acetic and formic acid. The sampling of method one, which is usually used for identification and quantification of VOCs, is done in accordance with ISO 16000-6 and ISO 16017-1 on Carbotrap® 202 multi-bed thermal desorption tube by subsequent identification and quantification with GC-MS. Method two is based on sampling on 2,4-dinitrophenylhydrazine (DNPH) cartridges, derivatisation, elution, identification and quantification of the derivatives with LC-MS/MS (liquid chromatography – mass spectrometry/mass spectrometry).

### 1 Introduction

Indoor air quality is important for human health and comfort. In order to preserve the indoor air quality, any contamination should be as low as possible. Many materials which are used for buildings and furniture including wood, glue and coatings, are possible sources of very volatile organic compounds (VOCs), like formic and acetic acid, volatile organic compounds (VOCs) and semi volatile organic compounds (SVOCs) [1 to 5]. Concentrations of these substances can increase considerably because of the very high air tightness and subsequently very low air exchange rates of modern buildings. Therefore, there is a need for a reliable method for identification and quantification of acetic and formic acid, which should be stable, robust, reproducible and comparable. This includes the on-site sampling as well as the analyses in the laboratories. Some possibilities for the identification of acetic acid already exist. One possibility is the quantification of acetic acid for example after sampling on Tenax® or Carbotrap® and thermal desorption-GC. Sampling of acetic and formic acid from test chamber air was done according to ISO 16000-6 [4] and as described in literature [1 to 5; 7]. Tenax® (based on a polymer of 2,6-diphenyl-p-phenyleneoxide) is mainly used for adsorption of substances in the retention range from n-hexane (C6) up to n-docosane (C22) on a nonpolar GC-column. For VOC Tenax® has a lower adsorption capacity. Furthermore Tenax® has a lower water adsorption capacity than activated carbon filter. Carbotrap® 202 multi-bed thermal desorption tube consists of Carbopack B and Carbopack C. Carbopack C is graphitized carbon black that is an ideal adsorbent resin for the trapping of organic analytes from C8 to the medium volatile compounds, smaller than C20. Carbopack B will efficiently trap and release VOC from C5 to C12 [6]. Therefore Carbotrap® tubes were used for the quantification of acetic acid in all experiments. With a second method, acetic and formic acid can be detected by the use of 2,4-dinitrophenylhydrazine (DNPH) cartridges for derivatization, elution and quantification of the derivates with LC-MS/MS (Flüssigkeitschromatographie – Massenspektrometrie/Massenspektrometrie).

### 2 Material and Methods

For comparison of both methods the limits of detection and quantification were determined for method I and method II as signal to noise ratio using a calibration solution in the lowest concentration range of 25 ng µl⁻¹ for method I and 0.5 ng µl⁻¹ for method II.
100 ml min^{-1} ranged between 0.2 and 5 l. The sample flow rate was methanol (for GC, suprasolv, Merck) as an internal standard. The sample volume of 1 l complies with 25 µg m^{-3}

The calibration line concentrations for acetic acid (96 %, suprapur, Merck) ranged from 5 ng µl^{-1} up to 400 ng µl^{-1}. A sample volume of 1 l complies with 25 µg m^{-3} in air and 25 ng µl^{-1} solvent on Carbotrap®.

The same procedure for producing standard solutions (derivatization of acetic and formic acid with DNPH at 80 °C) was used. As the hydrazides (derivates of acetic and formic acid) were commercially not available, they were produced in the in-house production and self-made derivatization on DNPH cartridge (Supelco). The procedure was as follows: 100 µl of standard solution with the concentration of approximately 10.500 ng µl^{-1} for acetic (96 %, suprapur, Merck) and 12.200 ng µl^{-1} for formic acid (98 to 100 %, suprapur, Merck) were given on a DNPH cartridge, derivatized at 80 °C for 8 h, eluted with acetonitrile (for LC-MS, lichrosolv, Merck), diluted and analysed with LC-MS/MS. The calibration line concentrations for formic acid ranged from approx. 0.5 ng µl^{-1} to 140 ng µl^{-1} and for acetic acid from approx. 0.25 ng µl^{-1} to 120 ng µl^{-1}. A sample volume of 60 l complies with 15 µg m^{-3} in air and 0.5 ng µl^{-1} in acetonitrile. For example a sample volume of 50 l corresponds to 30 µg m^{-3} in air and 1.0 ng µl^{-1} in acetonitrile. We can confirm the results from Possanzini et al [8]: The derivatization rate of these both acids increases with temperature and length of time. Eight hours at 80 °C lead to best results and the best recovery rates for the derivatization (results of these tests not shown).

Every sampling procedure was performed in duplicate. Using e.g. a FLEC pump (Chematec Company) of mostly 30 l at a collection rate of 500 ml min^{-1} and maintained with e.g. a FLEC pump (Chematec Company).

2.1 Method I

The air sample was drawn through a glass tube filled with Carbotrap®, 20 ng cyclodecane (Sigma-Aldrich) in 1 µl methanol (for GC, suprasolv, Merck) as an internal standard was added to the tubes before sampling. The sample volume ranged between 0.2 and 5 l. The sample flow rate was 100 ml min^{-1} and maintained with e.g. a FLEC pump (Chematec Company).

The calibration line concentrations for acetic acid (96 %, suprapur, Merck) ranged from 5 ng µl^{-1} up to 400 ng µl^{-1}. A sample volume of 1 l complies with 25 µg m^{-3} in air and 25 ng µl^{-1} solvent on Carbotrap®.

The GC system Agilent 6890 was equipped with a TDS from Gerstel (TDS – 2, splitless, start temperature 40 °C, temperature programme 40 °C/min to 290 °C isothermal for 5 min) and a cold injection system from Gerstel KAS – 4 (electronically controlled, splitless 1 min; temperature programme –100 °C at 12 °C/s to 290 °C isothermal for 5 min; liner deactivated glass tube with glass or quartz wool filling) coupled with the MS system Agilent MSD 5975. The column was DB 5 MS (50 m, 0.25 mm, 0.25 µm) with a constant flow of 1.5 ml/min and following oven programme: 40 °C 5 min, 5 °C/min to 150 °C for 1.5 min at 5 °C/min to 240 °C at 25 °C/min to 290 °C for 5 min. The identification was carried out with standards after substance identification with mass spectrum library NIST-02. The MS conditions were a 4.6 min solvent delay and a mass range of 25 to 400 m/z.

2.2 Method II

Method II is based on sampling on DNPH cartridges [10], derivatization of acetic and formic acid with DNPHI at 80 °C for 8 h, elution with acetonitrile (for LC-MS, lichrosolv, Merck) and quantification of the derivates (hydrazides) with LC-MS/MS.

The eluate was immediately analysed by LC-MS/MS using the following device parameters: The HPLC system HP1100 of Agilent Company (formerly Hewlett Packard), consists of a binary pump, gas-sampling valve, columns, thermostat, vacuum degasser and MS/MS (Esquire 6000 from Bruker) in the APCI mode. The column was an ULTRASEP ESD FS 125 x 2 mm (Sep Serv) and a mixture of acetonitrile/water 20/80 was used as solvent with an isocratic mode. The column was operated at 25 °C, run time 10 min and an injection volume of 5 µl. For assessment the software of Bruker Daltonics Quant-Analysis Rev. 1.6 and the specific ions for formic acid and acetic acid derivates m/z = 224.8 and m/z = 258.8 were used.

3 Results and Discussion

3.1 Results of method I after sampling on adsorbent and desorption with TDS, identification and quantification with GC-MS

Some specific problems of the identification and quantification of acetic acid after sampling from air on Carbotrap® are...
described below. A chromatogram of a standard solution for calibration with five compounds is given in Figure 1. The standard solution consists of a known concentration of acetic acid, chlorobenzene, cyclohexane, naphthalene and tribromobenzene. The last four compounds are internal standards, which are used for GC-MS quality control. The five compounds have the same concentration with approximately 200 ng µl⁻¹ and the integration of the acetic acid peak is not so reliable compared to the integration of the other compounds. The broad peak of acetic acid with a low response leads to mistakes by integration which results in higher measurement uncertainties by evaluation. Figure 2 (a magnification of Figure 1) points out the problems with the identification and quantification of acetic acid in air samples. The fronting of the acetic acid peak should be minimised. Using a split injection should improve the peak form but in contrast the analysis will get less sensitive. The consequence could be a much higher detection limit for such substances. The use of a polar column instead of a nonpolar is not allowed for the standard method I, according to DIN ISO 16000-6.

Sometimes acetic acid is quantified after sampling on Tenax® or Carbotrap® and thermal desorption as toluene equivalents with GC-MS. Figure 3 shows the unfavourable effect while using toluene equivalents for quantification of acetic acid. A subsequent calculation with a factor as described by Chan et al. [11] depends on the concentration of acetic acid and toluene, as shown in Figure 5. It is possible to identify acetic acid, but the quantification as toluene equivalents leads to minor concentrations. It must be taken into account that this underestimation increases with higher concentrations.

The calibration line for acetic acid after adsorption on Carbotrap® and desorption in the TDS is given in Figure 4. The concentration range is from 20 to 400 ng µl⁻¹. The correlation coefficient is 0.94 and the standard deviation of repeatability is below approx. 12 %. But not the entire calibration line is linear. The linear range is from 20 to 100 ng µl⁻¹. An exponential calibration curve fits better than a linear line, although a calculation with potential curve leads to higher uncertainty of measurement.

Results for the in-house repeatability (day by day and inter day) and standard deviation of repeatability (day by day and inter day) for two concentrations of acetic acid are calculated in Table 1. The highest standard deviation of day by day repeatability for the standard with \( c = 100 \text{ ng } \mu \text{l}^{-1} \) is 12.1 % and the highest standard deviation of inter day repeatability is 12.6 %.

The standard deviation of day by day and inter day repeatability for the second concentration with \( c = 50 \text{ ng } \mu \text{l}^{-1} \) acetic acid are smaller than for \( c = 100 \text{ ng } \mu \text{l}^{-1} \). The highest standard deviation of day by day repeatability amounts to 6.5 % and the highest standard deviation of inter day repeatability is 8.1 %.
3.3 Comparison of method I and method II

Some selected results to compare method I and II are given in Table 1. The table contains information about the compounds, limit of detection, limit of quantification, duration of the test and the sampling volume. The limits of detection and quantification were determined as signal to noise ratio with a calibration solution in the lowest concentration range.

Formic acid could not be analysed by method I, it is only possible by method II. It is obvious that the limits of detection and quantification depend on the sampling volume. This volume of method II is higher and results in lower limits of detection and quantification. Additionally the limits of detection and quantification, which were determined using calibration solutions, are significant lower for method II.

In contrast to method II, using method I the whole adsorbed sample will be desorbed without a dilution, injected and analysed. Summing up all effects, the limits of detection and quantification were significant lower for method II.

Regarding the two days for derivatization and elution, which are necessary for method II the procedure is twice as time consuming.

### Table 1. Comparison of both methods.

<table>
<thead>
<tr>
<th>compounds</th>
<th>method I</th>
<th>method II</th>
</tr>
</thead>
<tbody>
<tr>
<td>limit of detection</td>
<td>25 ng µl⁻¹ = 25 µg/m³</td>
<td>0.5 ng µl⁻¹ = 15 µg/m³ (60 l sampling volume)</td>
</tr>
<tr>
<td>limit of quantification</td>
<td>50 ng µl⁻¹ = 50 µg/m³</td>
<td>1.5 ng µl⁻¹ = 45 µg/m³ (60 l sampling volume)</td>
</tr>
<tr>
<td>duration</td>
<td>1 day</td>
<td>2 days</td>
</tr>
<tr>
<td>sampling volume</td>
<td>1 l</td>
<td>60 l</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>12.1 (c = 100 ng µl⁻¹, acetic acid)</td>
<td>14.9 (c = 5 ng µl⁻¹, acetic acid) (day by day)</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>12.6 (c = 100 ng µl⁻¹, acetic acid)</td>
<td>21.1 (c = 5 ng µl⁻¹, acetic acid) (inter day)</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>4.4 (c = 50 ng µl⁻¹, acetic acid)</td>
<td>14.2 (c = 5 ng µl⁻¹, formic acid) (day by day)</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>8.1 (c = 50 ng µl⁻¹, acetic acid)</td>
<td>21.8 (c = 5 ng µl⁻¹, formic acid) (inter day)</td>
</tr>
</tbody>
</table>

### Figure 5. Correlation of acetic acid (method II).

### Figure 6. Correlation of formic acid (method II).
Table 2. Uncertainty of measurement for formic acid and acetic acid (method II).

<table>
<thead>
<tr>
<th>Formic acid</th>
<th>Acetic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>theor. concentration in ng µl⁻¹</td>
<td>mean in ng µl⁻¹</td>
</tr>
<tr>
<td>6.9</td>
<td>6.1</td>
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<tr>
<td>13.7</td>
<td>13.2</td>
</tr>
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<td>27.5</td>
<td>27.2</td>
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<td>48.0</td>
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</tr>
<tr>
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<td>69.6</td>
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<td>89.2</td>
<td>90.7</td>
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<td>109.8</td>
<td>111.3</td>
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<tr>
<td>137.3</td>
<td>137.7</td>
</tr>
</tbody>
</table>

4 Conclusions

The described method II enables an appropriate identification and quantification procedure for formic acid and acetic acid in air. The interpretation of the chromatograms and consequently the identification and quantification of acetic acid is more workable and practicable than the analysis with GC-MS after sampling on Carbotrap® due to the evaluation of chromatograms. The identification of formic acid is impossible when applying the standard examination method I according to ISO 16000-6 [4] and ISO 16017-1 [12].

The uncertainties and recovery rates of both specified methods are comparable. The limits of quantification and detection are significantly lower for method II, but the sampling volumes are significantly higher for this method. Conditional on the results for the in-house repeatability (day by day and inter day), which were similar in a defined concentration range, the accuracy and the precision of method II could be confirmed in a cross-linked validation. Reproducibility and cross linked validation (accuracy) has to be checked in a method validation study (interlaboratory study). Robustness has to be studied in a multi factorial parameter approach (experimental study design) and should be done in a future study.

References


