

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

K. Wiegner, O. Hahn, W. Horn, M. Farke, S. Kalus, M. Nohr, O. Jann

Abstract Several construction and building materials, including wood, glue and coatings, are possible sources of very volatile organic compounds (VVOCs) 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. With 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).

Bestimmung der Ameisen- und Essigsäureemissionen in der Innenraumluft oder aus Bauprodukten

Zusammenfassung Viele Konstruktions- und Baumaterialien, wie Holz, Kleber und Anstriche, sind mögliche Quellen für leicht flüchtige organische Verbindungen (VVOc) und flüchtige organische Verbindungen (VOC), wie Ameisen- und Essigsäure. Bedingt durch die hohe Dichtigkeit und den damit verbundenen niedrigen Luftwechsel in neuen Gebäuden können die Konzentrationen dieser gesundheitsgefährdenden Substanzen beträchtlich ansteigen. Um das Risiko zu minimieren, sollen Emissionen aus Bauprodukten identifiziert und quantifiziert werden. Mit der üblichen Standardmethode, die auf einer Luftprobenahme auf Tenax® und anschließender Analyse mittels GC-MS basiert, können diese Säuren nicht ausreichend detektiert werden. Ziel dieser Arbeit ist der Vergleich von zwei unterschiedlichen Methoden zur Bestimmung von Essig- und Ameisensäure. Die Luftprobenahme der ersten Methode, die üblicherweise zur Identifizierung und Quantifizierung von VOC genutzt wird, wurde gemäß ISO 16000-6 and ISO 16017-1 auf Carbotrap® 202, ein mit mehreren Adsorbentien gepacktes Thermodesorptionsrohr, mit anschließender Identifikation und Quantifizierung mittels GC-MS durchgeführt. Die zweite Methode basiert auf einer Luftprobenahme mittels 2,4-Dinitrophenylhydrazin-(DNPH)-Kartuschen, Derivatisierung, Elution, Identifikation und Quantifizierung der Derivate mit LC-MS/MS (Flüssigkeitschromatographie – Massenspektrometrie/Massenspektrometrie).

Dr. Katharina Wiegner, Dr. Oliver Hahn,
Dr. Wolfgang Horn, Sabine Kalus,
Dipl.-Chem. (FH) Michael Nohr, Dr. Oliver Jann,

BAM Bundesanstalt für Materialforschung und
-prüfung, Berlin.

Dipl. Restaurator (FH) Matthias Farke,
Glasbau Hahn, Frankfurt am Main.

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 (VVOCs), like formic and acetic acid, volatile organic compounds (VOCs) and semi volatile organic compounds (SVOCs) [1 to 3]. 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 3; 5]. Tenax® (based on a polymer of 2,6-diphenyl-p-phenylenoxide) 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 VVOC 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 derivatives with LC-MS/MS [7 to 9]. These cartridges are normally used for detection of aldehydes and ketones, the analyses of these compounds is carried out after derivatization as described in ISO 16000-3 [10]. In this study the cartridges were used to sample small carboxylic acids. According to [7 to 9] the derivatization rate of these acids increases with higher temperature (80 °C) used for a longer period of time (8 hours).

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.

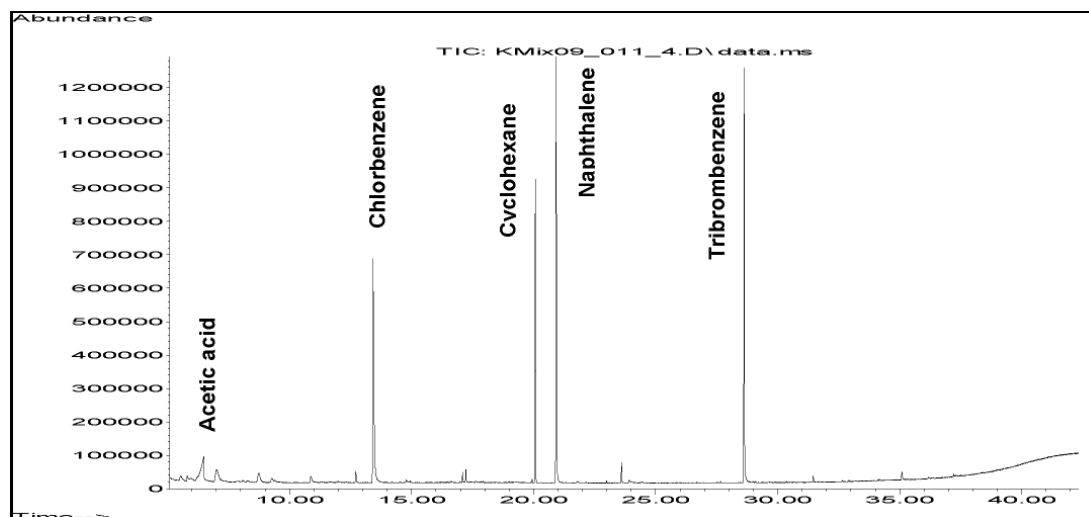


Figure 1. Standard mix with acetic acid, chlorobenzene, cyclohexane, naphthalene and tribrombenzene, $c = 200 \text{ ng } \mu\text{l}^{-1}$ (method I).

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 $5 \text{ ng } \mu\text{l}^{-1}$ up to $400 \text{ ng } \mu\text{l}^{-1}$. A sample volume of 1 l complies with $25 \mu\text{g m}^{-3}$ in air and $25 \text{ ng } \mu\text{l}^{-1}$ 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 5973. The column was DB 5 MS (30 m, 0.25 mm , $0.25 \mu\text{m}$) with a constant flow of 1.5 ml/min and following oven programme: 40°C 3 min, 5°C/min to 130°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 DNPH 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 same procedure for producing standard solutions (derivates of acetic and formic acid) was used. As the hydrazides are commercially not available, they were produced in the same way like real samples with a selected concentration of acetic and formic acid in the defined air volume or defined solution of acetic and formic acid in acetonitrile. Both hydrazides (derivates of acetic and formic acid: hydrazides (keto form) and hydrazones (enol form) [9]) for the calibration standards were in-house production and self-made derivati-

zation on DNPH cartridge (Supelco). The procedure was as follows: $100 \mu\text{l}$ of standard solution with the concentration of approximately $10.500 \text{ ng } \mu\text{l}^{-1}$ for acetic (96 %, suprapur, Merck) and $12.200 \text{ ng } \mu\text{l}^{-1}$ 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. $0.5 \text{ ng } \mu\text{l}^{-1}$ to $140 \text{ ng } \mu\text{l}^{-1}$ and for acetic acid from approx. $0.25 \text{ ng } \mu\text{l}^{-1}$ to $120 \text{ ng } \mu\text{l}^{-1}$. A sample volume of 60 l complies with $15 \mu\text{g m}^{-3}$ in air and $0.5 \text{ ng } \mu\text{l}^{-1}$ in acetonitrile. For example a sample volume of 30 l corresponds to $30 \mu\text{g m}^{-3}$ in air and $1.0 \text{ ng } \mu\text{l}^{-1}$ 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 of air at a collection rate of 500 ml min^{-1} , the loaded cartridges were stored in a refrigerator at approx. 6 to 8°C after sampling, derivatized at 80°C for 8 h and extracted with 1.6 ml acetonitrile for processing.

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 $125 \times 2 \text{ mm}$ (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 $5 \mu\text{l}$. 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 $m/z = 238.8$ 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

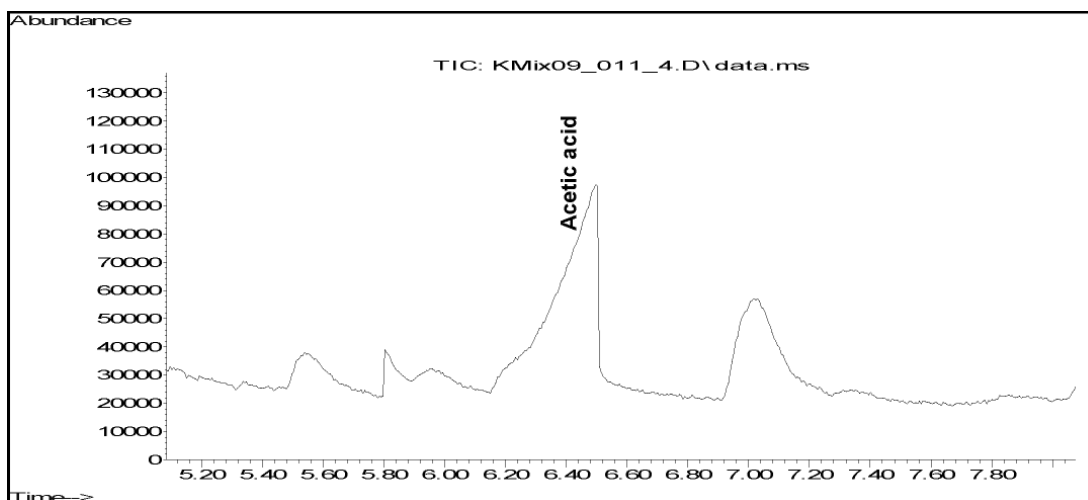


Figure 2. Acetic acid standard, $c = 200 \text{ ng } \mu\text{l}^{-1}$ (method I).

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 $200 \text{ ng } \mu\text{l}^{-1}$ 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 3. 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.

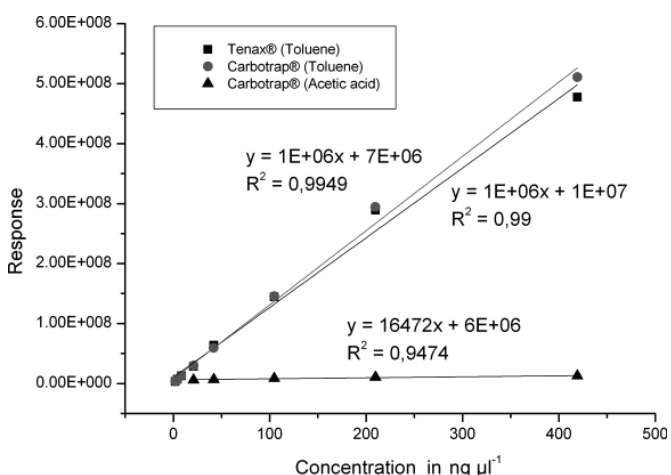


Figure 3. Comparison of toluene and acetic acid calibration lines (method I).

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 $400 \text{ ng } \mu\text{l}^{-1}$. 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 $100 \text{ ng } \mu\text{l}^{-1}$. 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 %.

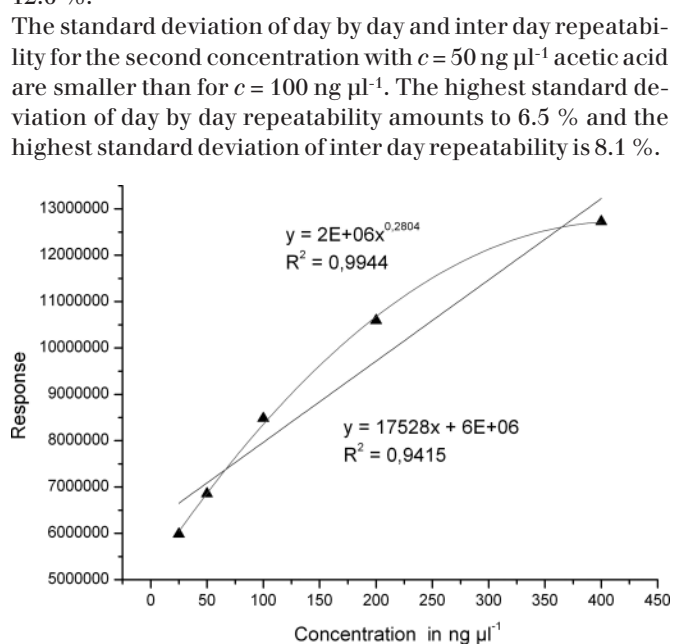


Figure 4. Calibration line for acetic acid standard from 20 to $400 \text{ ng } \mu\text{l}^{-1}$ (method I).

Table 1. Comparison of both methods.

	method I	method II
compounds	acetic acid, other VOC	formic acid and acetic acid
limit of detection	25 ng μl^{-1} = 25 $\mu\text{g}/\text{m}^3$	0.5 ng μl^{-1} = 15 $\mu\text{g}/\text{m}^3$ (60 l sampling volume)
limit of quantification	50 ng μl^{-1} = 50 $\mu\text{g}/\text{m}^3$	1.5 ng μl^{-1} = 45 $\mu\text{g}/\text{m}^3$ (60 l sampling volume)
duration	1 day	2 days
sampling volume	1 l	60 l
standard deviation in % (day by day)	12.1 (c = 100 ng μl^{-1} , acetic acid)	14.9 (c = 5 ng μl^{-1} , acetic acid)
standard deviation in % (inter day)	12.6 (c = 100 ng μl^{-1} , acetic acid)	21.1 (c = 5 ng μl^{-1} , acetic acid)
standard deviation in % (day by day)	4.4 (c = 50 ng μl^{-1} , acetic acid)	14.2 (c = 5 ng μl^{-1} , formic acid)
standard deviation in % (inter day)	8.1 (c = 50 ng μl^{-1} , acetic acid)	21.8 (c = 5 ng μl^{-1} , formic acid)

3.2 Results of method II after DNPH derivatisation identification and quantification with LC-MS

To control the derivatization of the acids to hydrazides the procedure was carried out on several times on each day. For acetic acid in Figure 5 and for formic acid in Figure 6, respectively the theoretical concentration (known concentration) is compared with the received and calculated concentration. For both acids the complete calibration lines are linear and the coefficient of determination is close to 1 and the linear slope is also near 1. As a consequence of these results it can be concluded, that the derivatization, elution and quantification for acetic and formic acid can be carried out repeatable and the recovery rates of this method are close to 100 %.

The range for the concentration line of acetic acid or formic acid is from 5 to 120 ng μl^{-1} or 5 to 140 ng μl^{-1} , respectively. Results for the in-house repeatability (day by day and inter day) and standard deviation of repeatability (day by day and inter day) for acetic and formic acid are calculated and shown in Table 1. The highest standard deviation of day by day repeatability is 14.9 % or 14.2 % and the standard deviation of inter day repeatability is 21.1 % or 21.8 % for acetic acid or formic acid, respectively.

The uncertainty of the measurement is strongly influenced by the considered concentration range. Table 2 lists the rela-

tive standard deviation for all concentration levels for formic and acetic acid and in addition the calculated results for relative standard deviation.

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

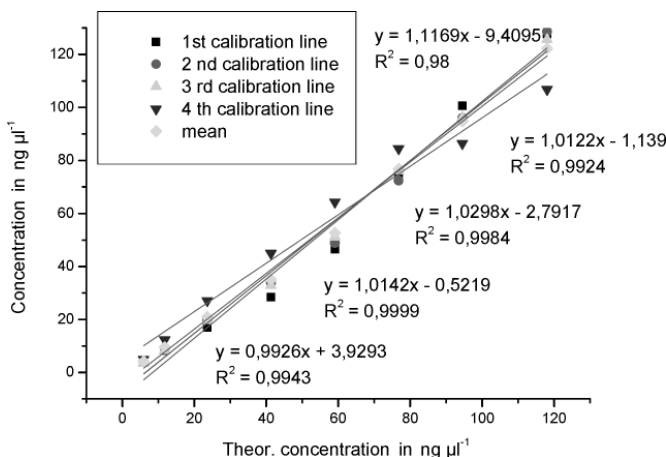


Figure 5. Correlation of acetic acid (method II).

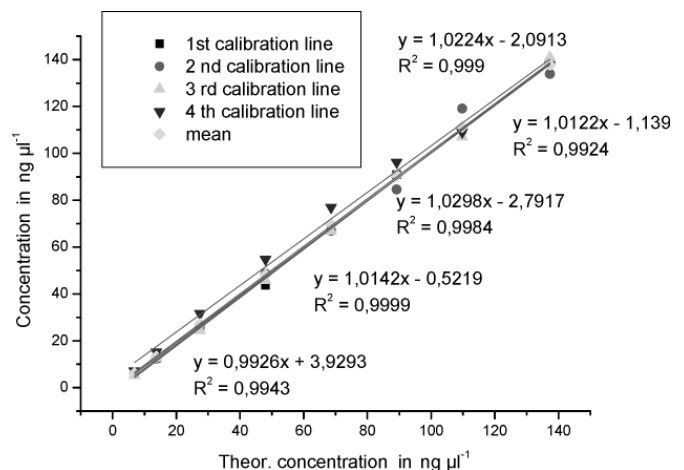


Figure 6. Correlation of formic acid (method II).

Table 2. Uncertainty of measurement for formic acid and acetic acid (method II).

Formic acid				Acetic acid			
theor. concentration in ng μl^{-1}	mean in ng μl^{-1}	standard deviation in ng μl^{-1}	standard deviation in %	theor. concentration in ng μl^{-1}	mean in ng μl^{-1}	standard deviation in ng μl^{-1}	standard deviation in %
6.9	6.1	0.8	13.7	5.9	4.2	0.6	15.5
13.7	13.2	1.4	10.5	11.8	9.5	2.0	21.1
27.5	27.2	3.1	11.3	23.6	20.9	4.3	20.8
48.0	48.2	4.8	10.0	41.4	35.0	7.0	20.1
68.6	69.6	4.9	7.1	59.1	52.6	8.0	15.2
89.2	90.7	4.8	5.3	76.8	76.7	5.4	7.0
109.8	111.3	5.3	4.8	94.5	94.8	6.0	6.3
137.3	137.7	2.9	2.1	118.1	122.2	10.4	8.5

consuming as for method I. The significantly higher sampling volume of at least 15 l in comparison to 1 l, tends to result in longer sampling time.

Summarizing both procedures: Method I is a screening method for acetic acid, it is common for identification and quantification of VOCs and should not be used for formic acid. These both acids formic and acetic acid can not be reliably analysed by GC-MS using a non-polar column. Method II is specific and selective for the identification and quantification of acetic and formic acid.

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.

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