Formic acid methyl ester

Method number	1
Application	Air analysis
Analytical principle	Gas chromatography (thermal desorption)
Completed in	September 2008

Summary

This analytical method can be used to determine gaseous formic acid methyl ester present in the air of workplaces in a concentration range from a tenth to twice the currently valid limit value in air by means of adsorption on Chromosorb™ 106 with subsequent thermal desorption [1, 2].

Sampling is performed by drawing ambient air through an adsorption tube packed with Chromosorb™ 106 using a suitable sampling pump. After thermal desorption, formic acid methyl ester is determined by gas chromatography with a flame ionization detector. The quantitative evaluation is based on a calibration function, whereby the concentrations of formic acid methyl ester in the calibration standards are plotted versus the peak areas obtained by an integrator.

Characteristics of the method

Precision:	Standard deviation (rel.):	$s = 0.8–2.1\%$
	Confidence interval:	$u = 2.1–5.4\%$
	at concentrations of 45.8, 117.6 and 228.3 mg/m^3 for $n = 6$ determinations	
Limit of quantification:	1.1 mg/m^3 at an air sample volume of 200 mL	
Recovery:	$\eta > 0.99$ (> 99%)	
Sampling recommendation:	Air sample volume:	0.2 L
	Flow rate:	0.3 L/h

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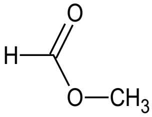
Formic acid methyl ester [CAS No. 107-31-3]



Synonym: Methyl formate

Formic acid methyl ester is a colorless, readily volatile liquid that is poorly soluble in water (molar mass 60.05 g/mol, density 0.976 g/cm³, melting point –99.8 °C, boiling point 31.8 °C). Its flash point is –32 °C and its vapor pressure is 640 hPa at 20 °C. The ester is miscible with water only to a limited extent (~ 1 : 3), whereby these mixtures break down relatively rapidly to methanol and formic acid, thus reversing the formation reaction. Formic acid methyl ester is highly flammable (explosion limits in air 5 to 23%) and has low water-endangering properties. It is used as a solvent for fats, oils, fatty acids, cellulose esters and acrylic resins. Formic acid methyl ester causes irritation to the eyes and the respiratory tract; contact with the liquid leads to skin irritation. The currently valid MAK value is 120 mg/m³ (50 mL/m³) [1]; the Occupational Exposure Limit is also 120 mg/m³ [2]. For short-term exposure formic acid methyl ester is classified in Peak Limitation Category II with an excursion factor of 4 [1, 2]. The detailed documentation of the toxicity of formic acid methyl ester is found in the „Toxikologisch-arbeitsmedizinische Begründungen von MAK-Werten“ [3].

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Contents

1
General principles

This analytical method can be used to determine gaseous formic acid methyl ester present in the air of workplaces in a concentration range from a tenth to twice the currently valid limit value in air by means of adsorption on Chromosorb™ 106 with subsequent thermal desorption [1, 2].

Sampling is performed by drawing ambient air through an adsorption tube packed with Chromosorb™ 106 using a suitable sampling pump. After thermal desorption, formic acid methyl ester is determined by gas chromatography with a flame ionization detector. The quantitative evaluation is carried out by means of comparison with calibration samples of known concentration. There is a linear relationship between the peak areas and the concentration.

2
Equipment, chemicals and solutions

2.1
Equipment

- Adsorption tubes made of stainless steel (6.3 mm × 90 mm, 5 mm inner diameter), packed with 300 mg Chromosorb™ 106 (e.g. PerkinElmer LAS, Rodgau, Germany)
- Sampling pump, suitable for a flow rate of 5 mL/min (e.g. PP-1, Gilian, USA)
- Gas chromatograph with thermal desorber and flame ionization detector (e.g. Turbomatrix ATD, PerkinElmer LAS, Rodgau, Germany)
- Sealing caps (e.g. Swagelok® with PTFE seals, PTFE or aluminum)
- Capillary column Wax-ETR: 30 m, 0.5 µm film thickness, 0.25 mm inner diameter (PerkinElmer LAS, Rodgau, Germany)
- Gas meter or stopwatch and soap bubble flowmeter
- Dynamic test gas facility according to VDI 3490, Issue 8 [4]
- Diluter/dispenser, Microlab M with 25 mL syringe (airtight), Hamilton Bonaduz AG, Switzerland

2.2
Chemicals

- Formic acid methyl ester, anhydrous, purity 99%, Sigma-Aldrich, Taufkirchen, Germany, Order No. 291056

- Methanol, p.a., purity > 99.9%, Merck KGaA, Darmstadt, Germany, Order No. 6009
- Gases for operation of the gas chromatograph:
  - Helium 4.6 (carrier gas), purity 99.996%
  - Purified or synthetic air (free of hydrocarbons)
  - Hydrogen 5.0 (purity 99.999%)

2.3

Pretreatment of the adsorption tubes

Before use, the adsorption tubes packed with Chromosorb™ 106 are heated for 10 minutes in the thermal desorber at 170 °C and then tested for blank values. Swagelok® or aluminum sealing caps are used to seal the tubes for storage.

2.4

Solutions

Approx. 25 mL of formic acid methyl ester are weighed exactly to 0.1 mg in a 100 mL volumetric flask. The flask is subsequently filled to its nominal volume with methanol (calibration solution, shown as an example in Table 1). The solution is used to generate the test atmosphere. The calibration solution is stored in the refrigerator.

The concentration of formic acid methyl ester in the calibration solution is 241.07 g/L.

Table 1 Test atmosphere concentrations and calibration masses.

Concentration of formic acid methyl ester: 219.5 mg/m³	
Sample volume [mL]	**Mass per sample [µg]**
1	0.22
10	2.20
20	4.39
40	8.78
60	13.17
80	17.56
100	21.96
120	26.35
140	30.74
160	35.13
180	39.52
200	43.91

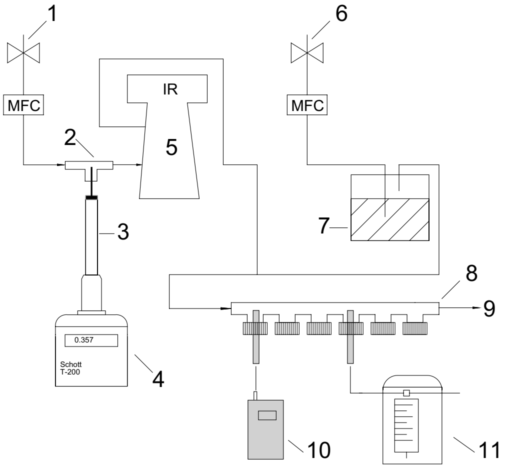

Fig. 1 Dynamic test gas facility. 1: Basic gas regulator, 2: Injector, 3: Piston, 4: Piston burette, 5: IR cuvette or buffer vessel, 6: Dilution gas regulator, 7: Humidifier, 8: Withdrawal manifold, 9: Excess test gas, 10: Sampling pump, 11: Diluter/dispenser

2.5

Test atmospheres and calibration standards

In the case of thermal desorption procedures it is advisable to carry out calibration with test atmospheres. There are different procedures to prepare test atmospheres [4, 5]. One possibility of preparing test atmospheres is continuous injection (see Fig. 1).

For this purpose the calibration solution (see Section 2.4) is continuously injected at a rate of 80 µL per hour into a basic gas flow of 400 mL per minute in a dynamic test gas facility. The desired concentration is then adjusted with a diluting stream of gas (in this case 1064 mL per minute). A diluter/dispenser is used to take aliquots from this calibration atmosphere in the range from 1 mL to 200 mL, and one adsorption tube is spiked with an aliquot in each case. This gives the test atmosphere concentrations or calibration masses shown in Table 1 at a total flow rate of 1464 mL/min. The calibration standards are equivalent to formic acid methyl ester concentrations in the range from 1.1 mg/m^3 to 220 mg/m^3 in the air sample based on an air sample volume of 200 mL.

3

Sampling and sample preparation

Stationary or personal sampling can be carried out. Before sampling, the adsorption tubes must be heated in the thermal desorber at 170 °C, as interferents from the sealing material of the PTFE sealing caps or from the ambient air can be adsorbed on the adsorbent phase when the adsorption tubes are stored for a longer period of time. The important parameters for the determination of the concentration of formic acid methyl ester in the air samples (temperature, air pressure, relative humidity) are documented in the sampling record. They are measured in the breathing zone in the case of personal sampling. It is important to ensure that the inlet aperture of the adsorption tube is freely accessible.

The adsorption tube is opened at the beginning of sampling. The sampling pump continuously draws the air to be investigated through the adsorption tube over a period of 40 minutes at a flow rate of 5 mL/min. In the case of longer sampling times the flow rate must be adjusted in such a way that the air sample volume does not exceed 200 mL. After sampling, PTFE caps are used to seal both ends of the loaded adsorption tubes. The samples should be analyzed within 48 hours after sampling has been completed. If the samples are to be stored over a longer period before analysis, then they must be sealed with Swagelok® screw caps with PTFE seals, but losses are to be expected in this case (see Table 4).

4

Operating conditions for gas chromatography

Apparatus:	Gas chromatograph Autosystem XL	
Column:	Material:	Quartz capillary
	Stationary phase:	WAX-ETR
	Length:	30 m
	Inner diameter:	0.25 mm
	Film thickness:	0.5 µm
Detector:	Flame ionization detector (FID), attenuation 16	
Detector temperature:	250 °C	
Detector gases:	Hydrogen 5.0 (flow rate 45 mL/min) Synthetic air (flow rate 450 mL/min)	
Temperature program:	$40\,^{\circ}\mathrm{C}\ (10\,\mathrm{min}) \xrightarrow{8\,^{\circ}\mathrm{C/min}} 120\,^{\circ}\mathrm{C}\ (10\,\mathrm{min})$	

Figure 2 shows a chromatogram of a calibration sample recorded under the conditions given above. Formic acid methyl ester elutes after 3.2 minutes under these conditions.

5

Analytical determination

To perform the gas chromatographic determination, the adsorption tubes prepared as described in Section 3 are heated to 170 °C in the thermal desorber and the adsorbed components are transferred by means of a carrier gas to the cold trap. After complete desorption, the split outlet is opened and the cold trap is heated.

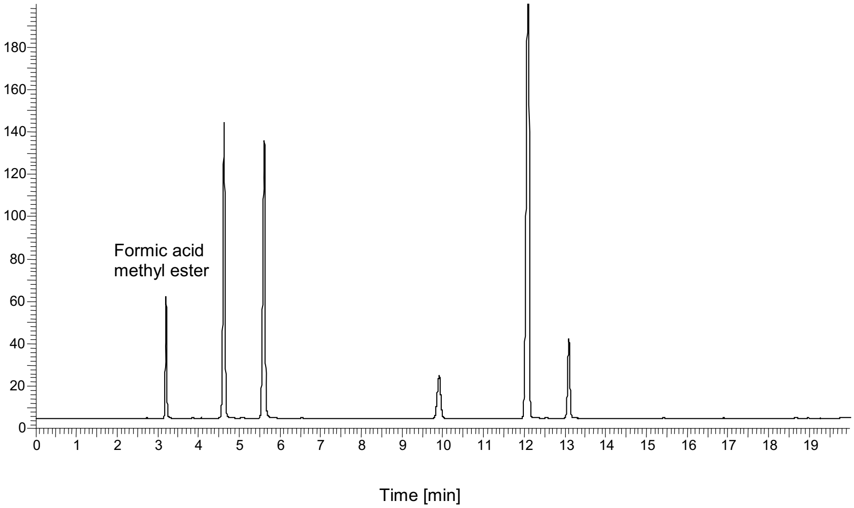

Fig. 2 Example of a chromatogram for the gas chromatographic determination of formic acid methyl ester (cf. Section 4 for the chromatographic conditions).

The sample is applied to the separation column in this manner as a narrow band of substance.

The thermal desorber is connected to the gas chromatograph via a deactivated quartz capillary. After preparation of the thermal desorber and the gas chromatograph (see Section 4), the calibration samples and the analytical samples are measured.

Thermal desorption conditions	
Apparatus:	Turbomatrix ATD (PerkinElmer LAS)
Desorption temperature:	170 °C
Desorption time:	10 min
Valve temperature:	200 °C
Temperature of transfer line:	200 °C
Length of transfer line:	1.5 m
Cold trap (adsorption):	–30 °C
Cold trap (injection):	300 °C
Heating rate:	40 °C/s
Packing of cold trap:	30 mg of Tenax TA™
Carrier gas:	Helium 4.6
Carrier gas pressure:	100 kPa
Input split:	40 mL/min
Desorb flow:	10 mL/min
Outlet split:	30 mL/min
Purge drying phase:	1 min at room temperature at 30 mL/min

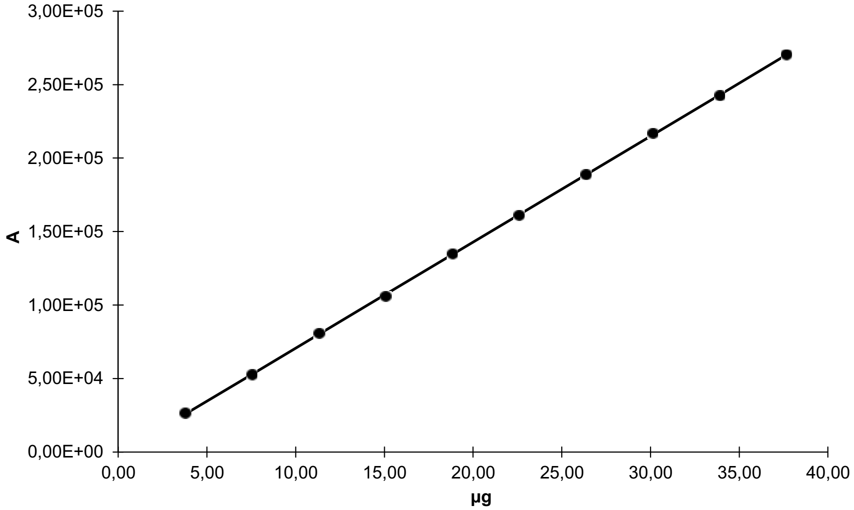

Fig. 3 Calibration graph for formic acid methyl ester; the masses [µg] are plotted versus the peak areas [A].

6
Calibration

The calibration standards should be spiked to give concentrations of between 0.1 and 2 times the air limit value [6]. The adsorption tubes are exposed to aliquots of 1, 10, 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mL of the test atmosphere generated as described in Section 2.5. This is equivalent to a concentration range from 1 mg/m^3 to 220 mg/m^3 at an air sample volume of 200 mL.

The calibration function is obtained by plotting the measured peak areas versus the masses loaded on the tubes in µg (see Table 1). The calibration curve is linear in the stated concentration range and should be regularly checked during routine analysis. A calibration standard of known concentration must be analyzed in each analytical series for this purpose. Figure 3 shows the calibration curve for formic acid methyl ester.

7
Calculation of the analytical result

Based on the determined peak areas, the corresponding mass (X) in µg per sample is obtained from the calibration curve. The corresponding concentration by weight (ρ) in mg/m^3 is calculated according to the following equation (1):

$$\rho = \frac{X}{V} \qquad (1)$$

equation (2) enables calculation of the value at 20 °C and 1013 hPa:

$$\rho_0 = \rho \times \frac{273 + t_a}{293} \times \frac{1013}{p_a} \tag{2}$$

The concentration by volume σ in mL/m^3 is calculated at t_a = 20 °C and p_a = 1013 hPa for formic acid methyl ester using the following equation:

$$\sigma = 0.401 \times \rho_0 \tag{3}$$

where:

ρ is the concentration by weight of formic acid methyl ester in mg/m^3
ρ_0 is the concentration by weight in mg/m^3 at 20 °C and 1013 hPa
X is the mass of formic acid methyl ester in the sample in µg
t_a is the temperature during sampling in °C
p_a is the air pressure at the sampling location in hPa
V is the air sample volume (calculated from the flow rate and the sampling time) in L

8
Evaluation of the method

The characteristics of the method were calculated as stipulated in EN 482 [6]. For this purpose test atmospheres with concentrations of 45.8 mg/m^3, 117.6 mg/m^3 and 228.3 mg/m^3 were generated. These test atmospheres were humidified with water to give a relative humidity of 65 to 70%. Six samples were taken from each concentration at room temperature (air sample volume 200 mL) and analyzed as described in Section 5. The limit of quantification was determined as stipulated in DIN 32645 [7] according to the blank value method.

Tubes were exposed to a humidified test atmosphere at a concentration of 113.4 mg/m^3 for the storage stability tests. The adsorption tubes were sealed with Swagelok® caps, stored at room temperature and analyzed over a period of four weeks.

8.1
Reliability

8.1.1
Precision

Three humidified test atmospheres of different concentrations were generated to determine the precision. Six samples with a volume of 200 mL were taken from

Table 2 Standard deviation (rel.) and confidence interval *u* for $n = 6$ determinations.

Test atmosphere concentration [mg/m³]	Standard deviation (rel.) [%]	Confidence interval *u* [%]
45.8	2.1	5.4
117.6	1.4	3.7
228.3	0.82	2.1

each test atmosphere. The samples were subsequently analyzed as described in Section 5. The results for precision are shown in Table 2.

8.1.2

Accuracy

The accuracy of the method was checked by comparative measurements. For this purpose test atmospheres were generated dynamically in two laboratories and then 200 mL each of these test atmospheres were drawn through each of a series of five adsorption tubes packed with Chromosorb ™ 106. The sampling tubes from the author's laboratory were evaluated in the examiner's laboratory and those prepared in the examiner's laboratory were evaluated in the author's laboratory. A calibration solution in methanol prepared by a dynamic test gas facility was used for the calibration procedure. The results of these comparative measurements are documented in Table 3. The mean recovery is 99.3%.

Table 3 Results of the comparative measurements ($n = 5$).

	Examiner I	Examiner II
Load [mg/m³]	61.7	57.7
Evaluation:		
Mean value [mg/m³]	61.1	56.9
Standard deviation (rel.) [%]	1.5	3.3
Recovery [%]	99.9	98.6

8.2

Limit of quantification

The limit of quantification was determined as stipulated in DIN 32645 [7] according to the blank value method. The limit of quantification is 1.1 mg/m^3 based on an air sample volume of 200 mL.

8.3

Recovery

Determination of the recovery is not possible in the case of thermal desorption procedures and simultaneous calibration using test atmospheres. The desorption rate was checked as part of the comparative investigations by two-fold heating of various adsorption tubes. It was greater than 99% at the stated concentration.

8.4

Storage stability

Investigations of the storage stability of the loaded adsorbents were carried out over a period of four weeks. For this purpose 200 mL of air from a humidified test atmosphere at a concentration of 113.1 mg/m^3 were drawn through adsorption tubes. The tubes were sealed with Swagelok® screw caps and stored at room temperature. No significant losses were detectable on the first two days (Table 4).

After a storage period of three days a mean recovery of approx. 90% was determined, which remained at this level until the end of the four weeks of storage stability tests. The results of the storage stability tests are shown in Table 4.

Table 4 Results of the storage stability tests.

Storage period [d]	Measured value [mg/m^3]	Recovery [%]
1	110.8	98.0
2	107.9	95.4
3	103.8	91.8
4	101.8	90.0
5	100.9	89.2
6	102.7	90.8
7	103.3	91.4
8	103.8	91.7
10	105.6	93.4
11	99.6	88.0
12	97.8	86.4
13	100.1	88.5
14	93.9	83.0
28	103.3	91.4
	$\overline{x}_{1-2d}$	96.7
	$\overline{x}_{3-28d}$	89.6

8.5
Interference

Interference to the determination of formic acid methyl ester on the separation column used may be caused by substances with the same retention time.

8.6
Capacity of the adsorbent

To test the capacity of the adsorbent, 500 mL of air from a test atmosphere with a concentration of 113 mg/m³ and at a temperature of 30 °C were drawn through two adsorption tubes connected in series. A breakthrough of less than 2% was determined in this case. The result confirms that the tubes used for the determination of the concentrations of formic acid methyl ester in the stated working range have sufficient capacity.

9
Discussion

The analytical procedure described here permits the determination of formic acid methyl ester in the air at the workplace in a concentration range from 45.8 mg/m³

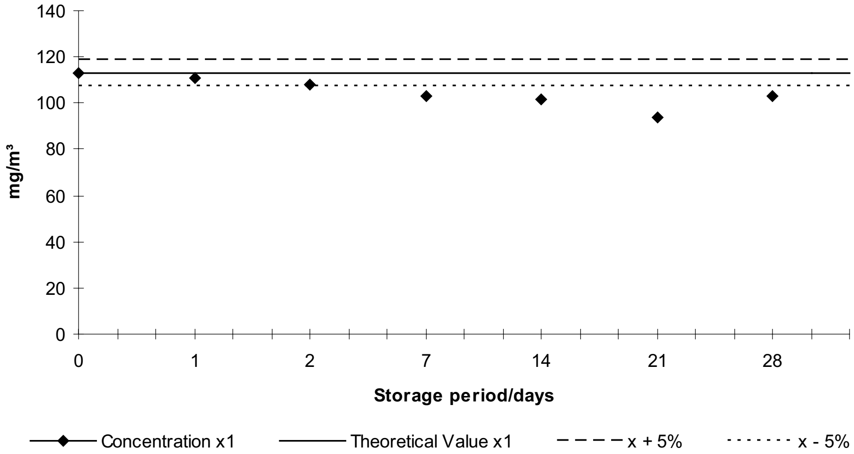

Fig. 4 Storage stability of formic acid methyl ester on Chromosorb™ 106 during a storage period of four weeks.

to 228.3 mg/m^3. Any air humidity present leads to slight losses when the standard settings are used for the desorption process. The losses can be minimized if the Chromosorb™ 106 is purged with moisture-free helium at 50 °C before the actual thermal desorption. However, a special extension of the equipment for purge drying is necessary for this purpose.

Formic acid methyl ester breaks down during storage; Fig. 4 shows a graph of the recovery during the storage stability tests. Interference is caused by components with the same retention time when a flame ionization detector is used together with the separation column specified here.

Calibration according to the continuous injection procedure is subject to interference due to the low boiling point of formic acid methyl ester. During the dosing phase uncontrolled spontaneous vaporization of the calibration solution occurs. The use of a compressed test gas mixture is preferable to the generation of a test gas mixture as stipulated in the procedure described above.

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