Federation of the Employment Accidents Insurance Institutions of Germany
(Hauptverband der Berufsgenossenschaften)
Centre for Accident Prevention and Occupational Medicine
Alte Heerstraße 111, 53757 Sankt Augustin
Expert Committee Chemistry

Carcinogenic substances	Order number: BGI 505-72E
Established methods	Issue: December 2002

Method for the determination of methoxyacetic acid

Method tested and recommended by the Berufsgenossenschaften for the determination of methoxyacetic acid in work areas after discontinuous sampling.
Both personal and stationary sampling can be conducted for the assessment of work areas.

Sampling with a pump and absorption in sodium hydroxide solution, ion chromatography (HPIC).

IUPAC name:	Methoxyacetic acid
CAS-No.:	625-45-6
Structural formula:	CH_3OCH_2COOH
Molar mass:	90.08 g/mol

The MAK-Collection Part III: Air Monitoring Methods, Vol. 10. DFG, Deutsche Forschungsgemeinschaft

ISBN: 978-3-527-31601-4

Sampling with a pump and absorption in a sodium hydroxide solution, ion chromatography after elution

Summary

This method permits the determination of methoxyacetic acid concentrations in work areas averaged over the sampling time after personal or stationary sampling.

Principle: A pump is used to draw a measured volume of air through a washing bottle containing sodium hydroxide solution. The absorbed methoxyacetic acid is determined by ion chromatography [1].

Technical data:

Limit of quantification:
absolute: 0.52 µg methoxyacetic acid
relative: 0.74 mg/m^3 methoxyacetic acid for a 140 L air sample, 10 mL absorption volume and an injection volume of 50 µL

Selectivity: The selectivity of the chromatographic method depends above all on the type of column and the separation conditions used. The separation conditions described here have proved reliable in practice.

Advantages: Personal sampling and selective determinations possible

Disadvantages: No indication of peak concentrations

Apparatus:
Pump
Gas meter or volumetric flow meter
Washing bottle
Ion chromatograph with UV detector

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:
- Pump, suitable for flow rates of 70 L/min, e.g. Gilian PP5 ex; supplier in Germany: e.g. DEHA Haan & Wittmer GmbH, D-71288 Friolzheim
- Non-leaking washing bottle "Absorber B 70 according to BIA", supplier e.g. GSM Schadstoffmesstechnik, D-41469 Neuss
- Gas meter or volumetric flow meter

For sample preparation and analysis:
- Volumetric flasks, 10 mL and 2000 mL
- Adjustable piston pipette, e.g. Multipette pro, from Eppendorf, D-22366 Hamburg
- Glass autosampler vials with crimp caps, e.g. Polyvial 1 mL, from Dionex, D-65510 Idstein
- Ultrapure water system for the preparation of ultrapure water, e.g. NANOpure ultrapure water system from Barnstead, supplier in Germany: Wilhelm Werner GmbH, D-51381 Leverkusen
- Ultrasonic bath

- Ion chromatograph
- UV detector

1.2 Chemicals and Solutions

- Methoxyacetic acid, 98%, e.g. from Sigma Aldrich, D-82018 Taufkirchen
- Sodium hydroxide solution, c = 0.1 mol/L, e.g. from Merck KGaA, D-64271 Darmstadt
- Hydrochloric acid, c = 1 mol/L, e.g. from Merck KGaA, D-64271 Darmstadt
- Tetrabutyl ammonium hydroxide solution, 40% in water, e.g. from Riedel de Haen, D-82024 Taufkirchen
- Ultrapure water

Eluent:	Solution of 0.15 mmol/L hydrochloric acid in ultrapure water. 0.3 mL of hydrochloric acid are pipetted into a 2000 mL volumetric flask, containing a few millilitres of ultrapure water. The flask is then filled to the mark with ultrapure water and shaken.
Absorption solution:	Sodium hydroxide solution, c = 0.1 mol/L
Calibration stock solution:	Solution of approx. 11.6 g/L methoxyacetic acid in absorption solution. 100 µL methoxyacetic acid (densitiy 1.175 g/mL) is pipetted into a 10 mL volumetric flask, weighed to the nearest 0.1 mg, and subsequently filled to the mark with absorption solution and shaken.
Calibration solutions:	Solutions of approx. 11.6 mg/L to 532 mg/L methoxyacetic acid in absorption solution (exact concentrations see Table 1). The volumes of calibration stock solution given in Table 1 are pipetted into a 10 mL volumetric flask containing a few millilitres of absorption solution. The flask is then filled to the mark with absorption solution and shaken. For an air sample volume of 140 L, these solutions cover a methoxyacetic acid concentration range from 0.8 mg/m^3 to 38 mg/m^3 air. The exact concentrations are listed in Table 1.

Table 1. Pipetting scheme for the preparation of calibration solutions of methoxyacetic acid.

Calibration solution No.	Volume calibration stock solution [µL]	Concentration of methoxy-acetic acid [mg /L]	Concentration of methoxy-acetic acid [mg/m^3] *
1	10	11.6	0.8
2	100	115.7	8.3
3	190	219.9	15.7
4	280	324.1	23.1
5	370	428.2	30.6
6	460	532.4	38.0

* for an air sample volume of 140 L

Validation stock solution: Solution of 16.61 g/L methoxyacetic acid in absorption solution. 166.1 mg Methoxyacetic acid is weighed into a 10 mL volumetric flask. The flask is then filled to the mark with absorption solution and shaken.

The calibration solutions are stable at room temperature for at least three weeks.
Before analysis of the sample, the calibration must be controlled daily e.g. with a solution containing methoxyacetic acid at a concentration of approx. 250 mg/L.

2 Sampling

The “Absorber B70” is filled with 10 mL absorption solution and connected to a pump. Pump and absorber are carried by a person during working hours or used in a stationary position. The flow rate is set at 1.16 L/min. Under these conditions sampling occurs in accordance with the definition of inhalable dusts. A sampling time of two hours corresponds to an air sample volume of approx. 140 L.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the absorber is quantitatively transferred to a 10 mL volumetric flask which is then filled to the mark with sodium hydroxide solution. After short shaking an aliquot is taken by means of a pipette and transferred to an autosampler vial. 50 µL of this solution is then injected into the ion chromatograph.

3.2 Operating conditions for ion chromatography

The method was characterized under the following experimental conditions:

Apparatus: Ion chromatograph DIONEX DX 120 with autosampler
Detector: UV detector, type VDM-2, from Dionex
Detection wave length: 205 nm
Pre-column: Micro-Guard Cation H-Cartridge, from Bio-Rad, D-80939 Munich
Column: Aminex HPx-87H, from Bio-Rad
Suppressor: AMMS-ICE II P/N 037107, from Dionex
Eluent: Hydrochloric acid (c = 0.15 mmol/L)
Flow rate: 0.6 mL/min
Flow rate suppressor: 1 mL/min
Injection volume: 50 µL
Temperature: Room temperature

4 Calculations

4.1 Calibration

Aliquots of 50 µL of each of the calibration solutions described in Section 1.2 are injected into the ion chromatograph. The peak areas determined for methoxyacetic acid are plotted against the weights of methoxyacetic acid contained in the corresponding solutions in order to construct the calibration curve. The calibration curve is linear in the specified concentration range.

4.2 Calculation of the analytical result

The concentration of methoxyacetic acid in the air sample is calculated according to equation (1):

$$c_w = \frac{w}{V \times \eta} \tag{1}$$

Where:
c_w is the concentration by weight of methoxyacetic acid in the air sample in mg/m^3
w is the weight of methoxyacetic acid in µg per sample determined from the calibration curve
V is the volume of the air sample in litres
η is the recovery

5 Reliability of the method

5.1 Accuracy and recovery

Accuracy in the minimum range of measurement according to DIN EN 482 [2] and recoveries were determined for three different concentrations (see Table 2).
Recovery was determined by doping 21 µL, 211 µL and 422 µL of the validation stock solution described in Section 1.2 into separate washing bottles “Absorber B 70”, containing 10 mL absorption solution and shaken. Subsequently, 140 L of laboratory air were drawn through the absorber at 1.2 L/min and processed as described in Section 3.1. Each concentration was determined in replicates of 6. The range of concentration examined in this way was between 2.5 and 50 mg/m^3.
Accuracy and recovery yielded the values in Table 2.

Table 2. Relative standard deviation s_{rel} and recovery for n = 6 determinations.

Validation concentration*	Relative standard deviation s_{rel} [mg/m^3]	Recovery
2.5	11.4	1.01
25.0	4.4	1.01
50.1	5.4	1.01

* for an air sample volume of 140 L

5.2 Limit of quantification

The limit of quantification was determined conform to the quick estimation of the limit of quantification according to the blank value method described in the DIN EN 32645 [3]. The standard deviation required for the calculation was determined in replicates of six injections of a methoxyacetic acid solution with a concentration of approx. 6 mg/L (0.43 mg/m^3 for an air sample volume of 140 L, respectively).
The absolute limit of quantification is 0.52 µg. This corresponds to a relative limit of quantification of 0.74 mg/m^3 for an air sample volume of 140 L, an absorption volume of 10 mL and an injection volume of 50 µL.

5.3 Selectivity

The selectivity of the chromatographic method depends above all on the type of column and the separation conditions used. The separation conditions described here have proved reliable in practice. Under the chromatographic conditions given, formic acid that might be present cannot be separated completely from the methoxyacetic acid. However, due to the use of the UV detector only high concentrations of formic acid interfere.

5.4 Shelf-life

Shelf-life of the samples is at least three weeks when stored in the refrigerator.

6 Discussion

The present method also permits the determination of acrylic acid concentrations in the air in the work areas.

7 References

[1] *Weiss, Joachim* (1995) Ion Chromatography, Second Edition. WILEY-VCH Verlag, Weinheim.
[2] Deutsches Institut für Normung e.V. (DIN) (1994) DIN EN 482 – Arbeitsplatzatmosphäre-Allgemeine Anforderungen an Verfahren für die Messung von chemischen Arbeitsstoffen. Beuth Verlag, Berlin.
[3] Deutsches Institut für Normung e.V. (DIN) (1994) DIN EN 32645 – Chemische Analytik-Nachweis-, Erfassungs- und Bestimmungsgrenze. Beuth Verlag, Berlin.

Author: *W. Krämer*