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Chloroacetic acids – Determination of mono-, di- and trichloroacetic acid in workplace air using high-performance liquid chromatography (HPLC-UV)

Air Monitoring Method – Translation of the German version from 2023

Keywords

chloroacetic acids; air analyses; analytical method; workplace measurement; hazardous substance; high-performance liquid chromatography; UV detection; HPLC-UV; quartz fibre filter; liquid desorption

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Abstract

The working group "Air Analyses" of the German Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK Commission) developed and verified the presented analytical method. This analytical method is a validated measurement procedure for the determination of monochloroacetic acid [79-11-8], dichloroacetic acid [79-43-6] and trichloroacetic acid [76-03-9] in workplace air in a concentration range of one tenth up to twice the currently valid occupational exposure limit values (OELVs) in Germany of 2.0, 1.1 and 1.4 mg/m^3, respectively. For sampling, a defined volume of air is drawn through a quartz fibre filter which is alkali impregnated with barium hydroxide and inserted into a sampling system for inhalable particles. The flow rate is set to 1 l/min and sampling is performed over a 2-hour period (which corresponds to a sampling volume of 120 l). The collected chloroacetic acids deposited on the filter are extracted by means of an aqueous phosphate buffer solution and analysed by high performance liquid chromatography with UV detection. Quantitative determination is based on multiple-point calibrations with external standards. For an air sample volume of 120 litres, the relative limit of quantification (LOQ) is in the range of 0.005 mg/m^3 for monochloroacetic acid and

trichloroacetic acid to 0.002 mg/m³ for dichloroacetic acid. The average recoveries of the three chloroacetic acids range from 88.6% to 101.5% and the expanded uncertainty is less than 29%.

Method number	1
Application	Air analysis
Analytical principle	High-performance liquid chromatography with UV detection (HPLC-UV)

1 Characteristics of the method

Precision:	Standard deviation (rel.):	
	Monochloroacetic acid:	s = 0.844 to 2.18%
	Dichloroacetic acid:	s = 0.464 to 2.79%
	Trichloroacetic acid:	s = 0.673 to 2.56%
	Expanded uncertainty:	
	Monochloroacetic acid:	U = 22.6 to 25.4%
	in a concentration range of 0.59 to 7.5 mg/m³ and for n = 6	
	Dichloroacetic acid:	U = 26.1 to 26.6%
	in a concentration range of 0.19 to 2.5 mg/m³ and for n = 6	
	Trichloroacetic acid:	U = 23.9 to 26.6%
	in a concentration range of 0.19 to 2.5 mg/m³ and for n = 6	
Limit of quantification:	Monochloroacetic acid:	0.05 mg/m³
	Dichloroacetic acid:	0.02 mg/m³
	Trichloroacetic acid:	0.05 mg/m³
	for an air sample volume of 120 l, an extraction volume of 3 ml and a sampling period of 2 h	
Recovery:	Monochloroacetic acid:	η = 88.6%
	Dichloroacetic acid:	η = 100.8%
	Trichloroacetic acid:	η = 101.5%
Sampling recommendations:	Sampling period:	120 min
	Air sample volume:	120 l
	Volumetric flow rate:	1 l/min

2 Description of the substances

Chloroacetic acids

Chloroacetic acids are α-chloro derivates of acetic acid and belong to the substance class of halogen acetic acids. Special characteristics are the low pK_a values in the range of 0.7 (ECHA 2022 c) to 2.8 (ECHA 2022 a). In contrast to acetic acid, they are classified as strong acids.

Monochloroacetic acid [79-11-8]

Monochloroacetic acid (MCA) is a colourless, crystalline solid with a pungent odour. It is a flammable, not easily ignitable compound, that is hygroscopic and readily soluble in water (ECHA 2022 a).

Apart from posing a hazard to water, acute and chronic health risks are also associated with MCA due to its strong corrosive effect. The current OELV and MAK value for monochloroacetic acid is 2 mg/m³ or 0.5 ml/m³ for the sum of

vapours and aerosols (AGS 2023; DFG 2023). The peak limitation has been assigned to Category I with an excursion factor of 2, resulting in a short-term value of 4 mg/m³. No risk of teratogenic effects need be feared, provided there is compliance with the OLEV or MAK value and the biological limit value (BLV) or BAT value (AGS 2023; DFG 2023).

Dichloroacetic acid [79-43-6]

Dichloroacetic acid (DCA) is a colourless liquid with a pungent odour. The substance is flammable and not easily ignitable, miscible with water as well as (very) poorly volatile (ECHA 2022 b). Apart from chemical synthesis, DCA has currently no further uses.

Like monochloroacetic acid, DCA poses a hazard to water and exhibits acute tissue-damaging effects due to the strongly corrosive and protein-precipitating properties. The OELV and MAK value is 1.1 mg/m³ for the sum of vapours and aerosols. The peak limit has been assigned to Category I with an excursion factor of 1 (AGS 2023; DFG 2023). DCA has been classified as Carcinogen Category 4 by the Commission (DFG 2023).

Trichloroacetic acid [76-03-9]

Trichloroacetic acid (TCA) is a white, crystalline solid with a weak acidic odour. The substance is not flammable, hygroscopic and readily soluble in water (ECHA 2022 c). Its use in the cosmetics sector and as a pesticide has been prohibited by the European Union (European Commission 2022; European Parliament and European Council 2009).

The substance has been classified as hazardous to water and can cause acute or chronic health issues (ECHA 2022 c). The current OELV and MAK value is 1.4 mg/m³ (AGS 2023; DFG 2023). The peak limit has been assigned to Category I with an excursion factor of 1. No risk of teratogenic effects need be feared, provided there is compliance with the OELV or MAK value and the biological limit value (BLV) or BAT value (AGS 2023; DFG 2023).

Physico-chemical data and evaluation criteria for the three chloroacetic acids are listed in Table 1.

Tab. 1 Substance data (ECHA 2022 a, b, c) and evaluation criteria for monochloroacetic acid (MCA), dichloroacetic acid (DCA) and trichloroacetic acid (TCA)

Name	MCA	DCA	TCA
CAS No.:	79-11-8	79-43-6	76-03-9
Molar mass [g/mol]	94.50	128.94	163.39
Aggregate state at 20 °C	solid	liquid	solid
Density at 20 °C [g/cm³]	1.64	1.56	1.61
Vapour pressure [Pa]	2.14[a)]	23.9[b)]	8[b)]
Melting point [°C]	63	13.5	56
Boiling point at 1013 hPa [°C]	190	194	196
Flash point [°C]	126	195	110
Evaluation criteria			
OELV, Germany (AGS 2023) / MAK value, Germany (DFG 2023)	2.0 mg/m³, 0.5 ml/m³	1.1 mg/m³, 0.2 ml/m³	1.4 mg/m³, 0.2 ml/m³
Peak Limit Category (excursion factor) (AGS 2023; DFG 2023)	I (2)	I (1)	I (1)

[a)] at 20 °C
[b)] at 25 °C

3 General principles

This analysis method permits the determination of MCA, DCA and TCA in workplace air. Chloroacetic acids or their salts occurring in gaseous and particulate form can be simultaneously determined with this method. The concentration range is one tenth to twice the currently valid OELV (see Table 1).

Sampling consists of a flow-regulated pump drawing a defined volume of air through an alkaline-impregnated quartz fibre filter that is located in a GSP sampling system with an intake cone for a flow rate of 1 l/min. The chloroacetic acids deposited on the filter in particulate form are measured by means of HPLC-UV after elution and neutralisation. An external calibration is used for quantitative evaluation.

4 Equipment, chemicals and solutions

4.1 Equipment

For sampling:

- Pump for personal sampling, flow rate of 1.0 l/min (e.g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- Personal sampling system for hazardous substances (PGP) using a GSP sampling head for the inhalable particle fraction with an intake cone for a flow rate of 1 l/min and suitable filter cassette (e.g. from DEHA Haan & Wittmer GmbH, 71296 Heimsheim, Germany)
- Quartz fibre filter Ø 37 mm (e.g. Whatman, from Cytiva Europe GmbH, 79111 Freiburg im Breisgau, Germany)
- Gas flow meter, suitable for a flow rate of 1 l/min

For sample preparation and analytical determination:

- Analytical balance with a measurement accuracy of 0.1 mg (e.g. from Sartorius AG, 37079 Göttingen, Germany)
- Piston pipettes (e.g. from Eppendorf SE, 22339 Hamburg, Germany)
- Microlitre syringes, 25 µl (e.g. 1702 RN, from Hamilton Bonaduz AG, Bonaduz, Switzerland)
- Tilting laboratory shaker
- Polypropylene (PP) vessels, 15 ml (e.g. from TPP Techno Plastic Products AG, Trasadingen, Switzerland)
- Volumetric flasks, 2 ml, 5 ml, 10 ml, 20 ml, 25 ml
- Measuring cylinders, 1 l
- Laboratory glass bottles, 1 l
- Erlenmeyer flasks, 50 ml
- Syringe filters, 0.2 µm pore size (e.g. Multoclear-13 PP, from CS-Chromatographie Service GmbH, 52379 Langerwehe, Germany)
- PP disposable syringes, 2 ml (e.g. from Büttner-Frank GmbH, 91058 Erlangen, Germany)
- PP autosampler vials with screw caps and PTFE-coated seals, 1.5 ml (e.g. from CS Chromatographie Service GmbH, 52379 Langerwehe, Germany)
- Glass Pasteur pipettes
- HPLC device with UV detector (e.g. Agilent 1100 series, from Agilent Technologies Deutschland GmbH, 76337 Waldbronn, Germany)
- HPLC column, C18, pH 2.5 to 8, aqueous phase, length 10 cm; inner diameter 2.1 mm; particle size 3 µm (e.g. Ultra Aqueous C18, from Restek GmbH, 61348 Bad Homburg, Germany)

4.2 Chemicals

- Monochloroacetic acid (MCA), purity 99% (e.g. from Sigma-Aldrich Chemie GmbH, 82024 Taufkirchen, Germany, Order No. C19627)
- Dichloroacetic acid (DCA), purity ≥ 99% (e.g. from Sigma-Aldrich Chemie GmbH, 82024 Taufkirchen, Germany, Order No. D54702)
- Trichloroacetic acid (TCA), purity ≥ 99.5% (e.g. from Merck KGaA, 64293 Darmstadt, Germany, Order No. 607-004-00-7)
- Ultrapure water ($\rho \geq 18.2$ MΩ × cm at 25 °C)
- Barium hydroxide solution, 0.15 mol/l (e.g. from Sigma-Aldrich Chemie GmbH, 82024 Taufkirchen, Germany, Order No. B4059)
- *ortho*-Phosphoric acid, purity 85% (e.g. from Merck Millipore, Merck KGaA, 64293 Darmstadt, Germany, Order No. 5.43828.0100)
- Potassium dihydrogen phosphate, purity ≥ 99.5% (e.g. from VWR International GmbH, 40764 Langenfeld, Germany, Order No. 153184U)

4.3 Solutions

The following solutions are prepared using the chemicals listed in Section 4.2:

Phosphate buffer: (75 mM of potassium dihydrogen phosphate in water):
The phosphate buffer is prepared by dissolving 10.2 g of potassium dihydrogen phosphate in 1 l of ultrapure water. For this purpose, potassium dihydrogen phosphate is weighed into a 1-l volumetric flask, which is filled to the mark with ultrapure water and shaken.

Dilute phosphoric acid: (8.5% in water):
ortho-Phosphoric acid (85%) is diluted 1:10 (v/v) with ultrapure water. For this purpose, 5 ml of water are placed into a 10-ml volumetric flask and 1 ml of *ortho*-phosphoric acid is added. The volumetric flask is then filled to the mark with ultrapure water and shaken.

Stock solutions: (80 mg of MCA/ml, 80 mg of DCA/ml, 80 mg of TCA/ml in phosphate buffer):
The stock solutions of the individual chloroacetic acids with a nominal mass concentration of 80 mg/ml in each case are prepared by weighing in the individual substances and subsequent dissolution in phosphate buffer. For this, 400 mg of the respective individual substance is weighed into a 5-ml volumetric flask. Then the volumetric flask is filled to the mark with phosphate buffer (75 mM) and shaken.

Working standard:
The working standard is prepared with appropriate dilutions of the stock solutions in phosphate buffer (75 mM). A defined volume of the stock solutions is added into a 10-ml volumetric flask according to Table 2. The volumetric flask is then filled to the mark with phosphate buffer (75 mM) and shaken. The concentrations of the chloroacetic acids can be found in Table 2. The working standard is prepared as two technical duplicates, whereby one working standard is used exclusively for the preparation of the calibration standards and the other for the preparation of the quality controls.

Tab. 2 Pipetting scheme for the preparation of the working standards and resulting nominal concentrations of the chloroacetic acids

Volume [ml]	Substance	Stock solution volume [µl]	Nominal concentration [µg/ml]
	MCA	120	960
10	DCA	40	320
	TCA	40	320

4.4 Calibration and control standards

Calibration standards are prepared in order to plot the calibration graphs. These are prepared as multiple standards.

Calibration standards:

The calibration standards are prepared by appropriate dilution of the working standard in a 5-ml volumetric flask. For this purpose, the volumes of the working standard, the barium hydroxide solution (0.15 mol/l) and the dilute phosphoric acid (8.5%) listed in Table 3 are added into a 5-ml volumetric flask, which is then filled to the mark with phosphate buffer (75 mM) and shaken.

Tab. 3 Pipetting scheme for the preparation of the calibration standard and resulting nominal concentrations of the chloroacetic acids

Calibration standard	Working standard	0.15 mol/l of barium hydroxide solution	Dilute phosphoric acid	Phosphate buffer	Concentration [µg/ml]		
	[µl]	[µl]	[µl]	[µl]	MCA	DCA	TCA
1	30	667	80	4223	5.76	1.92	1.92
2	60	667	80	4193	11.5	3.84	3.84
3	100	667	80	4153	19.2	6.40	6.40
4	150	667	80	4103	28.8	9.60	9.60
5	300	667	80	3953	57.6	19.2	19.2
6	500	667	80	3753	96.0	32.0	32.0
7	1000	667	80	3253	192	64.0	64.0
8	2000	667	80	2253	384	128	128

Control standards:

Four control standards (QC) are prepared by appropriate dilution of the working standard in a 5-ml volumetric flask. A control standard with a concentration at the lower limit of quantification (LLOQ), a control standard at low concentration (QCLow), a control standard at medium concentration (QCMed) and a control standard at high concentration (QCHigh) are prepared. For this purpose, the volumes of the working standard, the barium hydroxide solution (0.15 mol/l) and the dilute phosphoric acid (8.5%) listed in Table 4 are added into a 5-ml volumetric flask, which is filled to the mark with phosphate buffer (75 mM) and shaken.

Tab. 4 Pipetting scheme for the preparation of the control standards and resulting nominal concentrations of the chloroacetic acids

Control standard	Working standard	0.15 mol/l of barium hydroxide solution	Dilute phosphoric acid	Phosphate buffer	Concentration [µg/ml]		
	[µl]	[µl]	[µl]	[µl]	MCA	DCA	TCA
LLOQ	30	667	80	4223	5.76	1.92	1.92
QCLow	90	667	80	4163	17.3	5.76	5.76
QCMed	1000	667	80	3253	192	64.0	64.0
QCHigh	1500	667	80	2753	288	96.0	96.0

5 Sampling and sample preparation

5.1 Preparation of the sample carriers

The quartz fibre filter is impregnated before sampling. To this end, 200 µl of the 0.15 M barium hydroxide solution are uniformly distributed over the filter and dried in air. The time period between impregnation and sampling should be at least approx. 16 hours. Until sampling commences, the filter capsules remain sealed with the pertinent caps.

The batch of quartz fibre filters used must be checked for possible blank values.

5.2 Sampling

For sampling, a filter cassette equipped with a supporting sieve and an impregnated quartz fibre filter is inserted into the GSP sampling head (Riediger 2001) which is fitted with an intake cone for 1 l/min. Sampling is carried out over a time period of approx. two hours at a volumetric flow rate of 1 l/min to check the shift average, which results in an air sample volume of 120 litres. Sampling can be carried out as stationary or personal sampling. After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, it is advisable to discard the sample (DIN 2014). The filter cassette with the loaded filter is sealed with the caps, transported to the laboratory, prepared and analysed immediately.

It is advisable to include one blank sample (‘field blank’) per sample series. This differs from the analytical sample only in that no sample air was drawn through the filter. This blank sample is then stored and analysed in the same manner as the other samples.

5.3 Sample preparation

For sample preparation, the filters are each transferred into a 50-ml Erlenmeyer flask. After addition of 3 ml of phosphate buffer (75 mM) and 24 µl of dilute phosphoric acid (8.5%) the extraction is performed over the course of 30 minutes using the tilting laboratory shaker. Whereby it must be ensured that there is sufficient pivotal movement so that the filter is entirely wetted. Before analysis, the respective supernatant is filtered through a syringe filter with 0.2 µm pore size into an autosampler vial.

The blank sample (‘field blank’) is prepared in the same manner as the collected samples.

It is advisable to additionally prepare and analyse a reagent blank value (’lab blank’).

6 Operating conditions

Apparatus:	Agilent 1100 high performance liquid chromatograph
Separation column:	Restek Ultra Aqueous C18[a)]; length 100 mm; inner diameter 3 mm; particle size 3 µm
Column temperature:	30 °C
Detector:	UV detector (UV)
Wavelength:	205 nm
Mobile phase:	75 mM of phosphate buffer in ultrapure water
Flow rate:	0.5 ml/min
Injection volume:	10 µl
Run time:	approx. 5 min

[a)] Restek Ultra Aqueous C18 consists of a specific phase, that is suitable for the operation with 100% aqueous eluent.

7 Analytical determination

For the analytical determination, 10 µl of the samples prepared as described in Section 5.3 are each injected into the high-performance liquid chromatograph and analysed under the conditions described in Section 6. Depending on the chloroacetic acid to be determined, the relevant calibration graph is used for evaluation. If the measured concentrations are above the calibration range, then suitable dilutions using the eluent must be prepared and analysis must be repeated. Furthermore, the prepared blank sample ('field blank') and the reagent blank value ('lab blank') must be analysed in the same manner as the analytical samples.

8 Calibration

The calibration is carried out as described in Section 6 and 7 using multiple standards (see 4.4 calibration standards). A deviation of ± 15% from the nominal value is defined as an acceptance criterion. A deviation of ± 20% is accepted for the calibration point at the lowest concentration.

Control standards are used every working day for checking the calibration as well as in the context of sample sequences (bracketing of samples). The same acceptance criteria apply as described above for the calibration.

9 Calculation of the analytical result

Taking the air sample volume, the eluent volume, the dilution and the recovery into account, the concentration of chloroacetic acids in the workplace air is calculated according to Equation 1. If a recovery of 100 ± 5% in the range of one tenth to twice the limit value is determined, then no correction in Equation 1 should be carried out.

$$\frac{\left((c \times f_d) - c_{blank}\right) \times V \times 100}{V_{air} \times \eta} \quad (1)$$

where:

ρ	is the mass concentration of chloroacetic acid in the air sample in mg/m³
c	is the concentration of chloroacetic acid in the measured solution in mg/l
c_{blank}	is the concentration of the 'blank value' (mean value) in mg/l
f_d	is the dilution factor
V	is the volume of the eluent in litres (0.003 l in this case)
V_{air}	is the air sample volume in litres
η	is the recovery in %

10 Reliability of the method

The characteristics of the method were calculated as stipulated in DIN EN 482 (DIN 2021), DIN EN ISO 23861 (DIN 2023) as well as DIN 32645 (DIN 2008).

10.1 Repeatability

The repeatability was ascertained by multiple measurements of the control standards with n = 6 repetitions per concentration. The concentrations and the relative standard deviations determined are listed in Table 5.

Tab. 5 Data on the concentrations and the relative standard deviation for multiple measurements (n = 6) of the respective control standards for the determination of the precision

Reference standard	Concentration [µg/ml]			Relative standard deviation [%]		
	MCA	DCA	TCA	MCA	DCA	TCA
LLOQ	5.76	1.92	1.92	4.34	3.36	0.79
QCLow	17.3	5.76	5.76	0.44	0.64	0.11
QCMed	192	64.0	64.0	0.15	0.55	0.73
QCHigh	288	96.0	96.0	0.04	0.06	0.07

10.2 Recovery

The recovery was determined by spiking filters with MCA, DCA and TCA, followed by preparation and analysis.

The quartz fibre filters were prepared as described in Section 5.1. Six spiking solutions in phosphate buffer (75 mM) were prepared from the stock solutions (see Section 4.4) for spiking the filters and preparation of corresponding reference solutions. A spiking solution each with a low, medium and high concentration was prepared, which is equivalent to a measurement range of one tenth up to twice the OELV at spiked volumes of 300 µl of the spiking solution. The impregnated filters were each spiked with 300 µl of the spiking solution in a plastic filter holder. In order to investigate the influence of the relative humidity during sampling, nitrogen with either a relative humidity of approx. 30% or approx. 75% was drawn through the filters for two hours at a volumetric flow rate of 1 l/min in each case. A six-fold determination was carried out in each case.

The preparation of the filters was carried out as specified in Section 5 and 6. No evidence of any dependence on the relative humidity was found.

The mean recovery is 88.6% for MCA, 100.8% for DCA and 101.5% for TCA.

10.3 Method precision and expanded uncertainty

The method precision (sampling, preparation and analysis) was determined using the data for the recovery in Section 10.2. For this purpose, the relative standard deviations obtained from the six-fold determinations are calculated for both humidities and shown in Table 6. The expanded uncertainties were determined using the Excel sheet of the Institute for Occupational Safety and Health (IFA) of the German Social Accident Insurance (DGUV) (IFA n.d.) and are depicted in Table 6.

Tab. 6 Relative standard deviations and expanded uncertainties

Analyte	Concentration [µg/ml]	Concentration in air [mg/m³]	Rel. standard deviation at 33% rel. humidity [%]	Rel. standard deviation at 70% rel. humidity [%]	Expanded uncertainty [%]
MCA	23.4	0.59	2.18	1.04	25.4
	200	5.04	0.269	0.884	22.6
	299	7.53	0.975	0.884	24.1
DCA	7.71	0.194	2.79	1.07	26.6
	65.9	1.66	0.464	0.668	26.1
	98.9	2.49	0.841	0.659	26.5
TCA	7.57	0.191	2.56	1.57	25.8
	64.8	1.63	2.35	0.784	25.4
	97.1	2.45	1.31	0.673	23.9

10.4 Limit of quantification

During development of the method, the limit of quantification was calculated according to the calibration line method as specified in DIN 32645 (DIN 2008) with a statistical certainty of P = 99% and k = 3 for the six lowest concentrations. The relative limit of quantification for an air sample volume of 120 l (equivalent to a sampling period of 2 hours at a volumetric flow rate of 1 l/min) was calculated on the basis of the absolute limit of quantification (Table 7).

Tab. 7 Limits of quantification according to DIN 32645 (DIN 2008) (P = 99%; k = 3; uncertainty of the result: 33%; error probability: 1%)

Analyte	Absolute limit of quantification [µg/ml]	Relative limit of quantification[a)] [mg/m³]
MCA	1.96	0.05
DCA	0.644	0.02
TCA	1.93	0.05

[a)] on the basis of an air sample volume of 120 l and an extraction volume of 3 ml

10.5 Selectivity

10.5.1 Blank value

The selectivity of the method was based on six filter blank values. For this purpose, six impregnated filters without spiked analytes were subjected to a stream of nitrogen at a flow rate of 1 l/min (75% relative humidity) for two hours, then prepared and analysed as described in Section 5 and 6. A blank value with a signal area of 7.28 ± 1.04 mAU × min at 1.2 min was detected in resulting extracts, which does not correspond to any of the investigated chloroacetic acids (see Figure 1). The relative standard deviation for the signal area was determined as 14%. This signal must be taken into consideration, particularly for the determination of small concentrations of MCA.

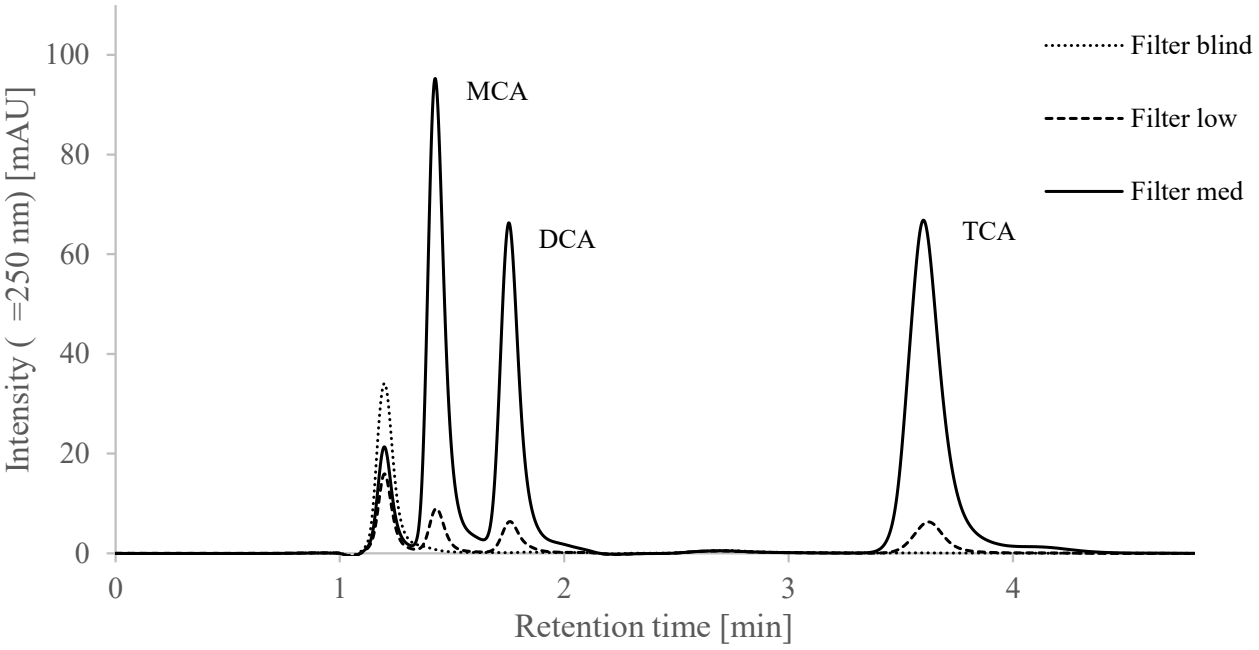

Fig. 1 Example of a chromatogram for a filter blank as well as filter samples with low and medium loading

10.5.2 Potential interference substances (selection)

Besides the chloroacetic acids, the potentially interfering substances propionic acid, 2-chloropropionic acid, 2,2-dichloropropionic acid, acetic acid, bromide and chloride, that may occur during sampling, were examined. The retention times of the substances are compared to those of the three chloroacetic acids in Table 8. Bromide and chloride show no signal and, therefore, do not interfere with the quantitative determination of the chloroacetic acids by means of HPLC-UV. The elution of 2,2-dichloropropionic acid with a retention time of 3.0 min is distinctly later than MCA and DCA and clearly before TCA. Therefore, 2,2-dichloropropionic acid does not interfere with the quantification of the three chloroacetic acids from an analytical point of view.

Tab. 8 Retention times of potential interference substances

Analyte	Retention time [min]
MCA	1.4
DCA	1.7
TCA	3.5
Propionic acid	3.6
2-Chloropropionic acid	1.9
2,2-Dichloropropionic acid	3.0
Acetic acid	1.8
Bromide	No signal
Chloride	No signal

For three potential interference substances, propionic acid, 2-chloropropionic acid and acetic acid, standards with known concentrations were prepared and the signal areas were compared to those of the corresponding chloroacetic acids:

- For a content of approx. 4.5 µg/ml of propionic acid in the measurement solution the area proportion is approx. 23% of the limit of quantification of TCA.
- For a content of approx. 1.2 µg/ml of 2-chloropropionic acid in the measurement solution the area proportion is approx. 23% of the limit of quantification of DCA.
- For a content of approx. 3.4 µg/ml of acetic acid in the measurement solution the area proportion is approx. 24% of the limit of quantification of DCA.

A quantification of the analyte is possible only when the area proportion of the respective interference substance does not exceed 20%.

10.6 Linearity

The linearity between the concentration and measurement signal was achieved for the selected concentration range (see Figure 2). A linear regression with a 1/x-weighting was applied.

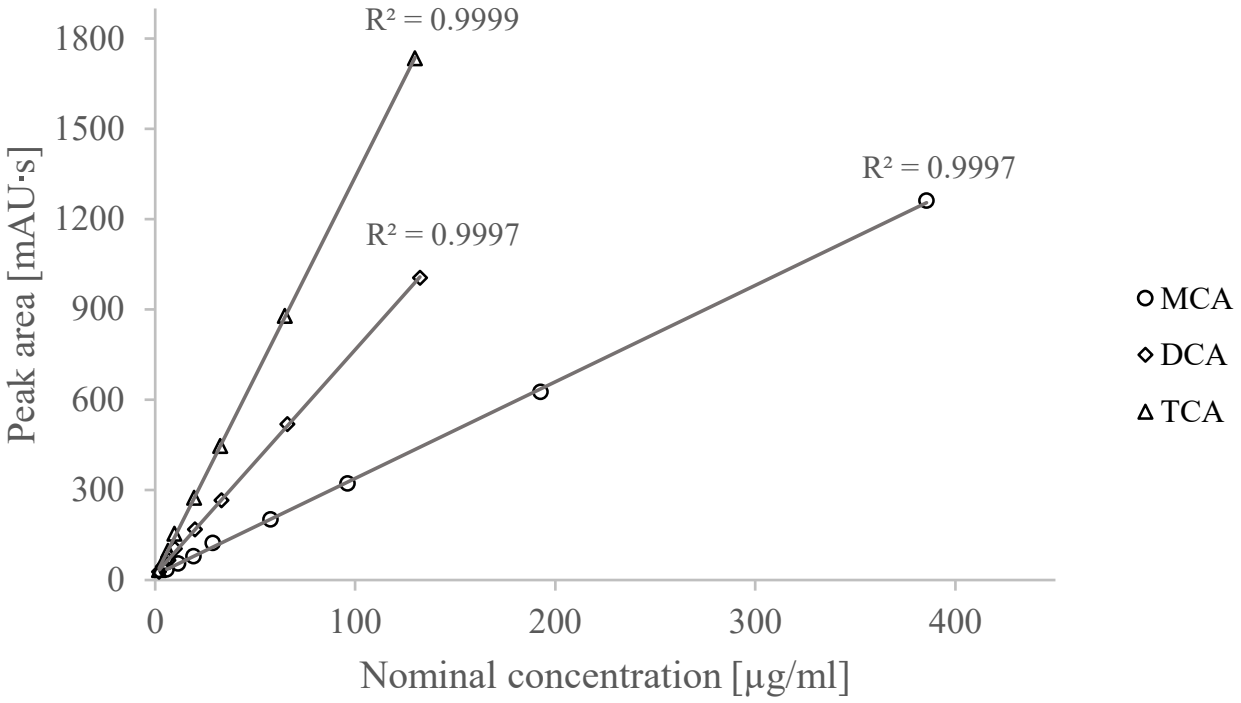

Fig. 2 Calibration functions for MCA, DCA and TCA

11 Discussion

The analytical procedure described here permits the determination of MCA, DCA and TCA in workplace air in a concentration range from one tenth to twice the currently valid OELVs of 2.0 mg/m^3 for MCA, 1.1 mg/m^3 for DCA and 1.4 mg/m^3 for TCA. By using an impregnated filter, chloroacetic acids occurring as aerosols as well as vapours are bound to the filter. The influence of the humidity was investigated at two relative humidities of approx. 30% and approx. 75%. The variation of the humidity had only a negligible influence on the measurement results.

Notes

Competing interests

The established rules and measures of the Commission to avoid conflicts of interest (www.dfg.de/mak/conflicts_interest) ensure that the content and conclusions of the publication are strictly science-based.

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