INTERNATIONAL STANDARD

**ISO
9486**

First edition
1991-08-15

Workplace air — Determination of vaporous chlorinated hydrocarbons — Charcoal tube/solvent desorption/gas chromatographic method

Air des lieux de travail — Détermination des hydrocarbures chlorés vaporeux — Méthode d'analyse par tube à charbon actif/désorption des solvants/chromatographie en phase gazeuse

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 9486 was prepared by Technical Committee ISO/TC 146, *Air quality*, Sub-Committee SC 2, *Workplace atmospheres*.

Annexes A, B and C form an integral part of this International Standard. Annex D is for information only.

Workplace air — Determination of vaporous chlorinated hydrocarbons — Charcoal tube/solvent desorption/gas chromatographic method

1 Scope

This International Standard specifies a charcoal tube/gas chromatographic method for the determination of the concentration of vaporous chlorinated hydrocarbons in workplace air.

The method is valid for the measurement of the concentrations of airborne vapours of any of the following compounds:

a) dichloromethane;

b) chloroform;

c) carbon tetrachloride;

d) 1,1-dichloroethane;

e) 1,2-dichloroethane;

f) 1,1-dichloroethene;

g) 1,2-dichloroethene;

h) 1,1,1-trichloroethane;

i) 1,1,2-trichloroethane;

j) trichloroethene;

k) 1,1,2,2-tetrachloroethane;

l) tetrachloroethene;

m) 1,2-dichloropropane;

n) chlorobenzene;

o) o-dichlorobenzene.

The method is valid for concentrations of airborne vapours of these compounds in the range from ap-

proximately 1 mg/m^3 to 1000 mg/m^3 (about 0,2 ml/m^3 to 200 ml/m^3; see 8.1) when sampling 10 litres of air.

NOTE 1   The upper limit of the useful range is set by the adsorptive capacity of the first section of the charcoal tube (5.1) used. This capacity is measured as a breakthrough volume of air, which should not be exceeded during sampling (see clause 6 and annex A).

The lower limit is set by a number of parameters, including the noise level of the detector (5.9), blank concentrations due to the contamination of the charcoal tube and carbon disulfide by the substance analysed, desorption efficiency (see annex B) and interference of the solvent peak in the gas chromatographic analysis.

The method is also valid for the measurement of airborne concentrations of mixtures of these compounds. In such cases, the unique properties of each compound have to be considered when determining the volume of air to be sampled and the gas chromatographic conditions to be used.

NOTE 2   When analysing chlorinated hydrocarbon mixtures with very large differences in concentrations and in which several compounds are present, the reproducibility and repeatability of the compounds of minor importance might be influenced.

The method has been validated for a selection of typical chlorinated hydrocarbons[1].

This procedure is compatible with low flow rate personal sampling equipment, and can be used for personal and fixed location sampling for obtaining time-weighted-average concentrations of chlorinated hydrocarbon solvent vapours in air. It cannot be used to measure instantaneous or short-term fluctuations in concentrations. Alternative on-site procedures, such as gas chromatography or infrared spectrometry, shall be used to measure rapidly changing concentrations.

1

Organic components which have the same or nearly the same retention time as the substance analysed during the gas chromatographic analysis will interfere. Interferences can be minimized by proper selection of gas chromatographic columns and programme conditions.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

ISO 6145-1:1986, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 1: Methods of calibration.*

ISO 6349:1979, *Gas analysis — Preparation of calibration gas mixtures — Permeation method.*

3 Principle

A known volume of air sample is passed through a glass or metal tube packed with activated charcoal. The organic vapours are adsorbed onto the charcoal.

The collected vapours are desorbed using a suitable solvent and analysed with a gas chromatograph equipped with a flame ionization detector or other suitable detector.

NOTE 3   For certain applications, in particular the analysis of carbon tetrachloride and chloroform, alternative detectors such as the electron capture detector may offer greater selectivity and sensitivity.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Chlorinated hydrocarbons, listed in clause 1, a) to o).

WARNING — Carbon tetrachloride and chloroform are suspect human carcinogens.

Avoid any exposure by inhalation or skin contact.

4.2 Carbon disulfide (CS_2), chromatographic quality, previously checked for compounds coincident with the substance analysed. If necessary, remove interfering compounds by percolation through silica gel (dried at 180 °C for 8 h under nitrogen) contained in a small glass column (600 mm × Ø int. 20 mm). This size of column will clean about 50 ml of carbon disulfide.

WARNING — Carbon disulfide vapour is toxic and highly flammable. Avoid any exposure by inhalation or skin contact. Use only in a well-ventilated fume cupboard. A carbon-dioxide fire extinguisher should be available at all times.

Dispose of small waste quantities of carbon disulfide in accordance with local regulations and accepted practices.

NOTE 4   Other desorption solvents may be used if their blanks and desorption efficiencies are adequate.

4.3 Activated coconut shell charcoal, particle size between 0,4 mm and 0,8 mm. Before packing the tubes, the charcoal shall be heated in an inert atmosphere, e.g. high purity nitrogen at 600 °C for 1 h. To prevent recontamination of the charcoal, it shall be kept in a clean atmosphere during its cooling to room temperature, storage and loading into the tubes.

NOTE 5   Suitable tubes containing pretreated coconut charcoal are commercially available (see 5.1).

4.4 Chlorinated hydrocarbons, standard solutions for the preparation of the calibration graph (see 7.1).

Prepare standard solutions of chlorinated hydrocarbons (4.1) gravimetrically and make serial dilutions from them to cover the range of the analysis. The concentration range of the analysis shall exceed the concentration range of the desorbed samples (see 7.2). As an example, a typical procedure for trichloroethene is described below.

Prepare standard solutions in carbon disulfide (4.2).

Prepare standard solutions of 1,2-dichloropropane in 15 % (V/V) acetone in cyclohexane.

4.4.1 Trichloroethene, standard solution, about 50 mg/ml.

Accurately weigh approximately 500 mg of trichloroethene in a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

4.4.2 Trichloroethene, standard solution, about 5 mg/ml.

Pipette 1 ml of the standard solution (4.4.1) into a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

4.4.3 Trichloroethene, standard solution, about 500 µg/ml.

Pipette 1 ml of the standard solution (4.4.2) into a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

4.4.4 Trichloroethene, standard solution, about 50 µg/ml.

Pipette 1 ml of the standard solution (4.4.3) into a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

4.4.5 Trichloroethene, standard solution, about 5 µg/ml.

Pipette 1 ml of the standard solution (4.4.4) into a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

4.5 Trichloroethene, standard matching solutions for checking the calibration graph (see 7.1).

4.5.1 Trichloroethene, standard matching solution, about 25 mg/ml.

Accurately weigh approximately 250 mg of trichloroethene in a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

4.5.2 Trichloroethene, standard matching solution, about 5 mg/ml.

Accurately weigh approximately 50 mg of trichloroethene in a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

5 Apparatus

Ordinary laboratory apparatus, and the following.

5.1 Charcoal tube, made of a glass tube with both ends flame sealed, 70 mm long with an outside diameter of 6 mm and an inside diameter of 4 mm, containing two sections of 0,4 mm to 0,8 mm of activated charcoal. The adsorbing section contains 100 mg of charcoal and the back-up section, 50 mg. The sections are separated and their contents are held in place with an inert material, e.g. glass wool plugs (preferably silanized).

The pressure drop across the tube shall not exceed 3 kPa (25 mmHg) at the maximum flow rate rec-

ommended for sampling (in this International Standard, 200 ml/min).

The glass tubes shall be held in suitable protective holders to prevent breakage. The desorption efficiency (D) for each batch of tubes shall be checked by one of the methods described in annex B. If the desorption efficiency is lower than 0,75 (75 %), the tubes shall not be used.

NOTES

6 The breakthrough volumes of dichloromethane, 1,2-dichloroethene and 1,2-dichloropropane are lower than for the other substances analysed. Consequently, a larger tube containing (400 + 200) mg charcoal is recommended for long-term sampling when these compounds are present.

7 1,1,2,2-Tetrachloroethane and 1,2-dichloropropane are unstable on coconut shell charcoal; petroleum-based charcoal should be used instead.

Clips shall be provided to hold the charcoal tube and connecting tubing to the wearer's lapel area.

IMPORTANT — Do not use charcoal tubes with any tubing upstream of the charcoal, as this may interfere with sampling and/or analysis.

NOTES

8 Instead of a commercial two-section tube, two single-section tubes in series may be used. This arrangement has the advantage that it is not necessary to store tubes at sub-ambient temperatures after sampling, to prevent migration of the trapped compounds from one section to the other.

9 Tubes meeting these requirements are commercially available, however they may also be made by the user.

5.2 Polyethylene end caps, for capping charcoal tubes (5.1). The caps shall fit the tubes tightly to prevent leakage.

5.3 Pump, with adjustable flow rate, capable of being worn by a person while carrying out his normal work, and capable of operating continuously for 8 h at the flow rate used (see clause 6). The volume of air sampled by the pump during the recommended sampling period shall be within 10 % of the calculated volume. The flow rate shall be constant within 5 % during the sampling period.

Calibrate the pump with a representative charcoal tube (5.1) in line, using the soap bubble meter (5.5).

The pump shall be in accordance with local safety regulations.

5.4 Plastics or rubber tubing, of length about 90 cm and of a diameter which is suitable for ensuring a leak-proof fit to both the pump and sample tube or tube holder, if used.

5.5 Soap bubble flowmeter, or other suitable device for calibration of the pump (5.3), of minimum capacity 100 ml.

NOTE 10   A soap bubble meter may not be appropriate for reciprocating pumps, i.e. those with non-constant flow.

5.6 Syringe, of capacity 10 µl, graduated in 0,1 µl.

5.7 Syringe, of capacity 50 µl, graduated in 0,1 µl.

5.8 Vials, fitted with polytetrafluoroethylene (PTFE)-lined septum caps, or glass-stoppered, of nominal capacity 2 ml or larger.

5.9 Gas chromatograph, with a flame ionization detector capable of detecting 5 ng of trichloroethene with a signal-to-noise ratio of at least 5 to 1.

NOTE 11   For the analysis of chloroform and carbon tetrachloride in the presence of large amounts of other chlorinated hydrocarbons, an electron capture detector should be used.

5.10 Gas chromatograph column, capable of separating the substance analysed from other components.

The suitability of the column shall be verified by testing with two or more columns of dissimilar packing to ensure the absence of interferences. Guidance on the choice of column is given in annex C.

6 Sampling

Attach the pump (5.3) to a charcoal tube (5.1), the ends of which are broken off, with the plastics or rubber tubing (5.4), placing the back-up section nearer to the pump.

When high relative humidity or high concentrations of other interferences are suspected, use a larger charcoal tube (400 mg or 800 mg with a 200 mg back-up section).

When using a second charcoal tube in series, ensure that the flow rate is set with a representative tandem set of tubes.

When used for taking individual samples, the tube shall be mounted vertically (in order to minimize channelling) in the worker's breathing zone, for example on his lapel. Attach the pump to the worker in a way that minimizes inconvenience. For fixed location sampling, choose a suitable sampling site.

Turn the pump on and adjust the flow rate so that the optimum sample volume is taken in the available time. Table 1 gives the air sample volumes for the various chlorinated hydrocarbons covered by this

International Standard and the equivalent 8 h sampling rates.

NOTE 12   For sampling over shorter periods, the flow rate may be increased in proportion, but should not exceed 200 ml/min. Thus, in all cases, sampling may be conducted for 10 min at 200 ml/min on a (100 + 50) mg tube.

Note and record the time, temperature, flow rate (or note the volume reading, if appropriate) and the barometric pressure when the pump was turned on.

NOTES

13   The sampling efficiency will be 100 %, provided that the sampling capacity of the charcoal is not exceeded. If this capacity is exceeded, breakthrough of vapour from the front section to the back-up section will occur. The breakthrough volume is defined and may be determined as specified in annex A.

The breakthrough volume varies with ambient air temperature, relative humidity, concentration of sampled vapour and other contaminants, and with the sampling flow rate. An increase in any of these parameters causes a reduction of the breakthrough volume. Some typical breakthrough volumes, which also vary with the type of substance analysed, are given in table 1.

14   Tubes containing larger quantities of charcoal may be used to sample larger volumes, and are recommended for long-term sampling of dichloromethane, 1,2-dichloroethene and 1,2-dichloropropane.

15   If 1,2-dichloropropane and 1,1,2,2-tetrachlorethane are present, two sample should be taken. With one of the samples, petroleum-based charcoal should be used instead of coconut shell charcoal (see also 5.1, note 7).

At the end of the sampling period, note and record the flow rate (or note the volume reading), turn the pump off, and note and record the time, temperature and barometric pressure.

Disconnect the sample tube and seal both ends with polyethylene end-caps (5.2). Place identifying labels on each tube.

If the samples are not to be analysed within 8 h, store them in a sealed metal or glass container placed either in dry ice or in a freezer maintained at − 20 °C, in order to minimize migration of the substance analysed.

NOTES

16   If two single-section charcoal tubes are used in series, they should be sealed separately, and it is not necessary to freeze them prior to analysis.

17   Test results are available for the relative decrease in concentration of three components after storage in a freezer at a relative humidity of 90 %. In a mixture of 560 mg of trichloroethene per square metre, 680 mg of tetrachloroethene per square metre and 3 970 mg of 1,1,1-trichloroethane per square metre, a decrease in the relative concentration was observed of respectively,

4,1 %, 5,7 % and 5,0 % after seven days;

4,4 %, 5,0 % and 6,4 % after 14 days;

8,3 %, 8,6 % and 9,5 % after 21 days.

Prepare sample blanks by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the sample tubes, except that no air shall be drawn through them. Label these as blanks.

Table 1 — Sample size and sampling rate

Substance analysed	Breakthrough volume data			Optimum sample		Bibliographic reference (annex D)
	Concentration mg/m³	Relative humidity (RH) %	Volume litres	Volume litres	8 h rate ml/min	
Dichloromethane	6 727	low	3,5	2	1)	[3]
	1 400	low	27	10	20	2)
	1 400	high	12	10	20	2)
Chloroform	485	low	>46	15	30	[3]
Carbon tetrachloride	322	low	>45	15	30	[3]
1,1-Dichloroethane	838	low	18	10	20	[3]
1,2-Dichloroethane	821	low	29	10	20	[3]
1,1-Dichloroethene	114	17	56	—	—	[4]
	114	95	3,7	—	—	[4]
	20	10	96	—	—	[4]
	10	85	7,2	—	—	[4]
	—	—	—	7	14	[3]
1,2-Dichloroethene	1 913	low	5,4	3	1)	[3]
				12	25	2)
1,1,1-Trichloroethane	3 979	low	9,5	6	12	[3]
1,1,2-Trichloroethane	108	low	>45	10	20	[3]
Trichloroethene	2 266	low	18,5	10	20	[3]
1,1,2,2-Tetrachloroethane3)	101	low	>44	10	20	[3]
Tetrachloroethene	2 749	low	21	10	20	[3]
1,2-Dichloropropane4)	85	90	20	4	1)	[3]
	865	90	6	4	1)	[3]
	—	—	—	14	30	2)
Chlorobenzene	704	low	>45	10	20	[3]
o-Dichlorobenzene	655	low	>46	10	20	[3]

NOTE — Except where stated otherwise, data refer to (100 + 50) mg of coconut shell charcoal.

1) Sampling rates below 10 ml/min are not recommended.

2) (400 + 200) mg charcoal tube.

3) NIOSH recommend petroleum-based charcoal.

4) NIOSH recommend petroleum-based charcoal; desorption solvent 15 % (V/V) acetone in cyclohexane.

7 Procedure

7.1 Calibration

Analyse each standard solution (4.4) for the substance analysed in triplicate by gas chromatography as follows.

Introduce, in a reproducible way, in the range 1 µl to 5 µl, a known aliquot of the standard solution into the gas chromatograph (5.9). The volume of the aliquot should be the same for each sample and standard in a set.

If overloading of the chromatographic system occurs, use smaller volumes of sample. In this case, the lower limit of detection is increased accordingly.

Prepare a calibration graph by plotting the areas of the peaks of the substance analysed, corrected for the blank value (carbon disulfide) against the concentrations of the standard solutions of the substance analysed, in micrograms per millilitre.

Check the calibration graph by analysing the standard matching solutions (4.5.1 and 4.5.2). If the difference is more than 5 %, carry out a new calibration.

7.2 Determination

Pipette 1,0 ml of desorption solvent (carbon disulfide) (4.2) into a 2 ml septum vial (5.8) and cap the vial immediately. Score the charcoal tube containing the sample in the front (largest) section and break open the tube. Remove the glass wool and discard it. Open the vial and transfer the front section of charcoal to the carbon disulfide in the vial and recap it. Agitate the vial occasionally over a period of 30 min to ensure maximal desorption. Repeat the same procedure for the second, back-up, section, using a different vial.

NOTES

18 When tubes containing more than (100 + 50) mg of carbon are used, a larger volume of carbon disulfide and a larger desorption vessel should be used pro rata (e.g. for 400 mg of charcoal, desorb with 4 ml of carbon disulfide).

19 For 1,2-dichloropropane, 15 % (V/V) acetone in cyclohexane is recommended as the desorption solvent, in order to get higher desorption. For all other chlorinated hydrocarbons, carbon disulfide should be used as the desorption solvent.

Inject the same volume of the sample as that used for preparing the calibration graph into the gas chromatograph. Determine the area of the peak of the substance analysed. Read from the calibration graph the corresponding mass concentration, in micrograms per millilitre, of substance analysed in the injected sample.

If the back-up section contains more than 10 % of the substance analysed contained in the front section, discard the sample as unreliable.

Analyse the blank tube in the same manner. Analyse a freshly prepared standard solution with each batch of samples.

8 Expression of results

8.1 Calculation

Calculate the mass concentration of substance analysed in the air sample, $\varrho(A)$, in milligrams per cubic-meter, using the equation

$$\varrho(A) = \frac{(\varrho_1 + \varrho_2 - \varrho_3)V_d}{D \cdot V}$$

where

ϱ_1 is the mass concentration of substance analysed, in micrograms per millilitre, in the solution prepared from the front section of the charcoal tube;

ϱ_2 is the mass concentration of substance analysed, in micrograms per millilitre, in the solution prepared from the back-up section of the charcoal tube;

ϱ_3 is the mass concentration of substance analysed, in micrograms per millilitre, in the solution prepared from both sections of the blank;

V is the volume, in litres, of the air sample;

V_d is the volume, in millilitres, of carbon disulfide used for desorption;

D is the desorption efficiency read from the D-curve, taking $(\varrho_1 + \varrho_2 - \varrho_3)V_d$ as the mass of substance analysed found (see annex B, B.2.6).

NOTES

20 If the concentration of the substance analysed has to be expressed at reference conditions (293 K and 101,3 kPa) the following equation should be used:

$$\varrho(A)_{corr} = \varrho(A) \times \frac{101{,}3(t + 273)}{p \times 293}$$

where

$\varrho(A)$ is the concentration of substance analysed, in milligrams per cubic metre, calculated above;

t is the mean temperature, in degrees Celsius, during sampling;

p is the mean atmospheric pressure, in kilopascals, during sampling;

101,3   is the standard pressure, in kilopascals;

273   is the standard temperature, in Kelvins;

293   is the equivalent, in Kelvins, of a temperature of 20 °C.

21   The volume fraction of substance analysed in the air sample, $\phi(A)$, in millilitres per cubic metre (ppm), is given by the equation

$$\phi(A) = \varrho(A)_{corr} \times \frac{24,0}{M}$$

where

$\varrho(A)_{corr}$ has the same significance as in note 20;

M is the relative molar mass, in grams per mole, of substance analysed;

24,0   is the volume of one mole of an ideal gas, in litres per mole, at 20 °C and 101,3 kPa.

8.2   Precision

A collaborative test[1] of a preliminary draft method, on which this International Standard is based, indicated that relative standard deviation, excluding between-laboratory and day-to-day variance components, was about 15 %, and, including these components, was about 25 %. Thus, when calculated in accordance with ISO 5725, repeatability was about 15 % and reproducibility, about 25 %.

NOTE 22   A collaborative test[2] of the NIOSH procedure[3], which is very similar to that described in this International Standard, and which included chloroform, carbon tetrachloride, 1,2-dichloroethane and trichloroethene, indicated that relative standard deviation, including between-laboratory and day-to-day variance components, was about 13 % under conditions where the sampling (pump) error was about 9 %. Relative standard deviation was worse for solvent mixtures and at low concentrations [5 % of OSHA[1] standard].

9   Test report

The test report shall include the following information:

a)   a reference to this International Standard;

b)   complete identification of the sample;

c)   the place and period of sampling;

d)   the barometric pressure and temperature;

e)   the desorption efficiency;

f)   the test result and the method of expression used;

g)   any unusual features noted during the determination;

h)   any other information relevant to the method.

---

1)   Occupational Safety and Health Association.