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

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

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Foreword

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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 9487 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.

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Workplace air — Determination of vaporous aromatic 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 aromatic hydrocarbons in workplace air.

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

a) benzene;

b) toluene;

c) ethylbenzene;

d) *m*-xylene;

e) *o*-xylene;

f) *p*-xylene;

g) styrene (vinylbenzene);

h) cumene (isopropylbenzene);

i) 1,2,3-trimethylbenzene;

j) 1,2,4-trimethylbenzene;

k) 1,3,5-trimethylbenzene;

l) 4-*tert*-butyltoluene;

m) 3-methylstyrene;

n) 4-methylstyrene;

o) isopropenylbenzene.

The method is valid for concentrations of airborne vapours of these compounds in the range from approximately 1 mg/m^3 to 1 000 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 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. The method may be applicable for other substituted monocyclic aromatic hydrocarbons, but its validity has to be tested.

NOTE 2 When analysing aromatic 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 aromatic 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 aromatic 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.

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.

4 Reagents

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

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

WARNING — Benzene is a recognized human carcinogen.

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 of interest. 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 3 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 4 Suitable tubes containing pretreated coconut charcoal are commercially available (see 5.1).

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

Prepare standard solutions of aromatic 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 toluene is described below.

Prepare standard solutions in carbon disulfide (4.2).

If the standard solution (4.4.1) has to be stored (for not longer than 1 week), prepare it in *n*-heptane.

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

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

4.4.2 Toluene, 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 Toluene, 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 Toluene, 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 Toluene, 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 Toluene, standard matching solutions for checking the calibration graph.

If the standard solutions (4.5.1 and 4.5.2) have to be stored (for not longer than 1 week); prepare them in *n*-heptane.

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

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

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

Accurately weigh approximately 50 mg of toluene 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 recommended 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.

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

5 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.

6 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 7 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 toluene with a signal-to-noise ratio of at least 5 to 1.

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 aromatic hydrocarbons covered by this International Standard and the equivalent 8 h sampling rates which vary as a function of the relative humidity and the presence of light hydrocarbons (see table 2).

NOTE 8 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.

NOTE 9 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.

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.

NOTE 10 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.

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.

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 shall 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.

Table 1 — Sample size and sampling rate

Substance analysed	Breakthrough volume data			Optimum sample		Bibliographic reference (annex D)
	Concentration mg/m^3	Relative humidity (RH) %	Volume litres	Volume litres	8 h rate ml/min	
Benzene	149	low	> 46	12	25	[5]
4-*tert*-Butyltoluene	112	low	44	—	—	[5]
Cumene	480	low	46	10	20	[5]
Ethylbenzene	917	low	35	—	—	[5]
Isopropenylbenzene	940	low	> 46	—	—	[5]
3-Methylstyrene and 4-methylstyrene	952	low	36	—	—	[5]
Styrene	1 710	low	21	5	10	[5]
Toluene	2 245	low	12	12	25	[5]
Xylene	810	low	34	12	25	[5]

NOTE — In these breakthrough experiments, air of low relative humidity and containing the substance analysed at the stated concentration was drawn at 0,2 l/min through six 100 mg sections (of diameter 4 mm) of coconut-shell charcoal in parallel. The effluent streams were recombined and monitored with a total hydrocarbon analyser or a gas chromatograph. At the breakthrough volume, the concentration of substance analysed in the effluent was 5 % of the challenge concentration.

Table 2 — Optimum sampling rate during 8 h as a function of the relative humidity and the presence of light hydrocarbons

Values in millilitres per minute

Composition of vaporous hydrocarbons in the air	Relative humidity		
	30 %	50 %	80 %
Benzene: 5 ml/m^3	> 200	> 200	125
Benzene: 5 ml/m^3 and in the presence of hydrocarbons $C_5 - C_6$: 80 ml/m^3 (equivalent C_6)	> 200	> 185	85
Benzene: 5 ml/m^3 and in the presence of hydrocarbons $C_5 - C_6$: 250 ml/m^3 (equivalent C_6)	80	70	40

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.

NOTE 11 When charcoal 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).

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, $\varrho(\mathrm{A})$, in milligrams per cubic-meter, using the equation

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

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 (less than 10 % of ϱ_1);

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 $(\varrho_1 + \varrho_2 - \varrho_3)V_\mathrm{d}$ as the mass of substance analysed found (see annex B, B.2.6).

NOTES

12 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:

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

where

$\varrho(\mathrm{A})$ 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.

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

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

where

$\varrho(\mathrm{A})_\mathrm{corr}$ has the same significance as in note 12;

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

In a collaborative test[1], a preliminary draft charcoal tube method, on which this International Standard is based, was compared with an independent diffusive tube test method [2] for measuring the occupational exposure to benzene. The results of the two methods could not be distinguished statistically.

In a similar collaborative test ([3] and [4]), for measuring the occupational exposure to styrene, again the results of the two methods could not be distinguished statistically. The mean coefficient of variation of the pumped charcoal tube results was 10 % and that of the diffusive tube results, 8 %.

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.

Annex A
(normative)

Determination of breakthrough volume

A.1 General

The breakthrough volume for the charcoal tube is the volume of a vapour-in-air sample that can be passed through the front section of the charcoal tube before the eluting concentration of aromatic hydrocarbon vapour reaches 5 % of the applied test concentration.

The breakthrough volume is dependent, among other things, on the concentration of the sampled vapour, the relative humidity and the ambient air temperature.

A.2 Reagents

Dynamic standard atmospheres of aromatic hydrocarbon vapour in air

Prepare dynamic standard atmospheres of aromatic hydrocarbon vapour in air by dilution of a metered flow of aromatic hydrocarbon liquid with a metered flow of air (see ISO 6145-1) or dynamically with permeation tubes (see ISO 6349).

A.3 Apparatus

Ordinary laboratory apparatus, and the following.

A.3.1 Charcoal tube, consisting of a single section, containing 100 mg of charcoal (4.3) (see 5.1).

A.3.2 Flowmeter, range 20 ml/min to 200 ml/min.

A.3.3 Flame ionization detector..

A.4 Determination

A.4.1 Assemble a sampling train consisting of a dynamic standard-atmospheres generator (A.2) delivering a concentration equivalent to the current exposure limit for the substance analysed (e.g. 375 mg/m^3 for toluene), a charcoal tube (A.3.1) with 100 mg of charcoal, the flowmeter (A.3.2) and the detector (A.3.3).

Pass the gas through the sample train at a known constant rate between 20 ml/min and 200 ml/min. Use a value in this range which is suitable for the sampling rate intended (see clause 6). Note the time that the flow was initiated.

When the aromatic hydrocarbon vapour begins to emerge, the detector will show a response. Continue the measurement until a plateau corresponding to the input concentration is reached, or until the response is determined to be caused principally or totally by the aromatic hydrocarbon used. Determine the time at which 5 % of the plateau value has been reached.

A.4.2 Usually, the dead volume of the sampling train is low in comparison with the breakthrough volume. If this is not the case, determine the dead volume by repeating the determination with an empty tube in the sampling train and correct the result accordingly.

A.4.3 Determine the effect of moisture on the breakthrough volume by humidifying the gas stream to approximately 80 % relative humidity and repeating the test described in A.4.1. Humidify the gas stream by diluting, in a ratio of 1:4 by volume, a primary gas stream of aromatic hydrocarbon, at a concentration of 50 mg/m^3, with a stream of moist air at 100 % relative humidity. The moist air is prepared by passing clean air through a series of water bubblers or tubes. Do not pass the aromatic hydrocarbon gas stream through water.

NOTE 14 The relative humidity specified (80 %) is a practical value; it does not imply that the method is invalid at higher relative humidities, provided due attention is given to the restriction on sampling volumes at high humidity (see clause 6).

A.5 Expression of results

Calculate the breakthrough volume by multiplying the flow rate, expressed in litres per minute, by the elapsed time, in minutes, from zero until the moment at which 5 % of the plateau value corresponding to 10 mg/m^3 has been reached.

Annex B

(normative)

Determination of desorption efficiency

B.1 General

The desorption efficiency for the charcoal tube is the mass recovered from the tube divided by the mass applied.

The desorption efficiency of aromatic hydrocarbon solvents from charcoal can vary with the type and batch of charcoal, the concentration of adsorbed vapour and the laboratory.

Thus, it is necessary to determine, for each batch of charcoal, the desorption efficiency over the expected concentration range of the substance analysed. Two methods are provided for the determination of desorption efficiency. The method using calibration gases (B.2) is the more stringent method.

Some typical desorption efficiencies are given in table B.1.

Table B.1 — Desorption efficiency data [5]

Substance analysed	Desorption efficiency	Mass of substance analysed on charcoal section mg
Benzene	0,96	0,088
	0,98	0,18
	0,98	0,35
4-*tert*-Butyltoluene	1,06	0,27
	1,10	0,54
	1,04	1,09
Cumene	1,06	0,86
	1,01	1,73
	1,03	3,46
Ethylbenzene	1,05	2,17
	1,08	4,34
	1,05	8,67
Isopropenylbenzene	0,91	0,69
	0,91	1,38
	0,93	3,57
3-Methylstyrene and 4-methylstyrene	0,82	2,41
	0,88	4,82
	0,91	9,64
Styrene	0,87	2,17
	0,88	4,24
	0,93	8,49
Toluene	0,98	1,13
	1,00	2,25
	0,99	4,51
Xylene	0,99	2,60
	0,99	5,21
	0,99	10,4

NOTE — In the experiments, 100 mg sections of coconut-shell charcoal were doped with the substance analysed, either neat or as a solution in hexane.

These samples were desorbed with 0,5 ml or 1,0 ml of carbon disulfide and analysed by gas chromatography.

B.2 Determination using calibration gases

B.2.1 Reagents

Dynamic standard atmospheres of aromatic hydrocarbon vapour in air.

See annex A, A.2.

B.2.2 Apparatus

B.2.2.1 Pump, as described in 5.3.

B.2.2.2 Charcoal tube, as described in 5.1.

B.2.2.3 Calibrated flowmeter..

B.2.3 Procedure

Determine the desorption efficiency at five different tube loading levels in the range of the analysis. The load range of the analysis shall exceed the load range of the samples. A typical range is 10 µg to 50 mg of the substance analysed, and an example for toluene is given below. Preferably use three charcoal tubes (B.2.2.2) for each load level. Prepare a standard atmosphere of toluene (B.2.1) at a concentration of 750 mg/m^3. Sample 10 litres of this atmosphere at a sampling rate of 20 ml/min, measuring the flow rate with a calibrated flowmeter (B.2.2.3).

NOTES

15 The sample may be passed through the charcoal tube and flowmeter from a pressurized source, or drawn through the tube by a calibrated pump (B.2.2.1).

16 The same conditions as during sampling (see clause 6) should be chosen for sample volume, flow, temperature and relative humidity. If necessary, warm up, cool or humidify the sample (see annex A, A.4.3).

The maximum pressure drop across the tube specified in 5.1 shall be observed. The sampling efficiency is assumed to be 100 %. At the end of the sampling period, remove, seal and label the tubes as specified in clause 6.

Repeat the procedure specified above but take smaller sample volumes, i.e. sample 0,5 litre, 1,0 litre, 2,0 litres and 5,0 litres of the 750 mg/m^3 standard atmosphere.

NOTE 17 For compounds other than toluene, standard atmosphere concentrations and sampling flow rates typical of those for sampling (see table 1) should be used, but it should be ensured that the breakthrough volume is not exceeded (see annex A).

B.2.4 Blank test

Select one charcoal tube from the same batch of tubes as that used for sample collection and subject it to the same handling procedure as the tubes used for sampling, except that no air is drawn through. Label this as a blank.

B.2.5 Determination

Analyse the loaded tubes and the blank tube, as specified in 7.2.

B.2.6 Expression of results

Calculate the desorption efficiency, D, using the equation

$$D = \frac{(\varrho_4 + \varrho_5 - \varrho_6)V_\mathrm{d}}{m}$$

where

ϱ_4 is the mass concentration of substance analysed, in micrograms per millilitre, in the solution prepared from the front section of the charcoal tube;

ϱ_5 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_6 is the mass concentration of substance analysed, in micrograms per millilitre, in the solution prepared from both sections of the blank (B.2.4);

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

m is the total mass of substance analysed, in micrograms, loaded on the charcoal tube (see B.2.3).

Prepare a graph (D-curve) by plotting the desorption efficiencies at the five different loading levels against the corresponding masses of substance analysed $(\varrho_4 + \varrho_5 - \varrho_6)V_\mathrm{d}$.

B.3 Determination using aromatic hydrocarbon solutions

NOTE 18 This method does not take into account ambient conditions prevailing during sampling.

B.3.1 Reagents

B.3.1.1 Aromatic hydrocarbons, standard solutions in carbon disulfide (4.2).

Prepare standard solutions of aromatic hydrocarbons gravimetrically and make serial dilutions from them, to cover the range of the analysis. The concentration range of the analysis shall be such that suitable aliquots can be taken for loading tubes as described in B.3.3. The following typical procedure for toluene is given as an example.

B.3.1.1.1 Toluene, standard solution, about 500 mg/ml.

Accurately weigh approximately 5 g of toluene in a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

B.3.1.1.2 Toluene, standard solution, about 50 mg/ml.

Pipette 1 ml of standard solution (B.3.1.1.1) into a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

B.3.1.1.3 Toluene, standard solution, about 5 mg/ml.

Pipette 1 ml of standard solution (B.3.1.1.2) into a 10 ml one-mark volumetric flask. Dilute to the mark with carbon disulfide and mix well.

B.3.2 Apparatus

B.3.2.1 Pump, as specified in 5.3.

B.3.2.2 Syringe, of capacity 20 µl.

B.3.3 Procedure

Determine the desorption efficiency at five different tube loading levels in the range of the analysis. The load range of the analysis shall exceed the load range of the samples. A typical range is 10 µg to 50 mg of the substance analysed, and an example for toluene is given below. Preferably use three charcoal tubes (B.2.2.2) for each load level.

By means of the syringe (B.3.2.2), slowly inject 20 µl of the toluene standard solution (B.3.1.1.1) into the glass wool preceeding the front section of the charcoal sampling tube connected to the operating pump (B.3.2.1). Allow the pump to operate continuously for approximately 10 min at a rate of about 200 ml/min.

Repeat the procedure specified above with 20 µl of the other toluene standard solutions (B.3.1.1.2 and B.3.1.1.3).

B.3.4 Blank test

Carry out a blank test using the procedure specified in B.3.3, but inject 20 µl of pure carbon disulfide.

B.3.5 Determination

Analyse the loaded tubes and the blank tube as specified in 7.2.

B.3.6 Expression of results

Calculate the desorption efficiencies and plot a graph as specified in B.2.6.

NOTE 19 If the desorption efficiency at the sample load level is less than 0,75 (75 %) the result is strictly invalid. The method should be checked for optimum performance and a fresh sample should be taken whenever possible. If this is not possible, the result should be corrected for desorption efficiency and it should be mentioned in the test report that the result is only approximate.