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Ambient air — Determination of particle-phase polycyclic aromatic hydrocarbons by high performance liquid chromatography

Air ambiant — Détermination des particules d'hydrocarbures aromatiques polycycliques par chromatographie liquide à haute performance

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

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ISO 16362 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 3, *Ambient atmospheres*.

Introduction

Several polycyclic aromatic hydrocarbons (PAHs) are considered to be potential human carcinogens. PAHs are emitted into the atmosphere primarily through combustion of fossil fuel and wood. Two- and three-ring PAHs are typically present in urban air at concentrations ranging from ten to several hundred nanograms per cubic metre (ng/m^3); those with four or more rings are usually found at concentrations of a few nanograms per cubic metre or lower. PAHs possess saturation vapour pressures at 25 °C that range from 10^{-2} kPa to less than 10^{-13} kPa. Those with vapour pressures above 10^{-8} kPa may be substantially distributed between the gas phase and particle-associated (particulate) phase in the atmosphere. The distribution between phases depends on ambient temperature, humidity, types and concentrations of PAHs and particulate matter, and residence time in the air. PAHs, especially those having vapour pressures above 10^{-8} kPa, tend to vaporize from particle filters during sampling.

This International Standard allows the determination of low volatility, particle-bound PAHs, in contrast to ISO 12884[1] which allows the measurement of PAHs in the gas phase. This International Standard allows the use of a range of sampler flowrates, and requires the use of high performance liquid chromatography (HPLC) with the detection carried out by either fluorescence detection or UV absorption.

Ambient air — Determination of particle-phase polycyclic aromatic hydrocarbons by high performance liquid chromatography

1 Scope

This International Standard specifies sampling, clean-up and analysis procedures for the quantitative determination of low volatility (particle-bound) polycyclic aromatic hydrocarbons (PAHs) in ambient air. For sampling, a low-volume or a medium/high-volume sampling device may be used. Sampling times between 1 h and 24 h are possible. The sampling volume flowrates can range from 1 m^3/h to 4 m^3/h ("low volume sampler") or from 10 m^3/h to about 90 m^3/h ("medium/high-volume sampler"). In any case, the linear face velocity at the collection filter should range between about 0,5 m/s and 0,9 m/s.

The method has been validated for sampling periods up to 24 h. The detection limits for single PAHs and the standard deviations resulting from duplicate measurements are listed in 9.2 and Annex D respectively.

This International Standard describes a sampling and analysis procedure for PAH that involves collection from air onto a filter followed by analysis using high performance liquid chromatography usually with fluorescence detector (FLD). The use of a diode array detector (DAD) is possible. The combination of both detector types is also possible (see Annex B). Total suspended particulate matter is sampled.

Generally, compounds having a boiling point above 430 °C (vapour pressure less than 10^{-9} kPa at 25 °C, e.g. chrysene, benz[*a*]anthracene) can be collected efficiently on the filter at low ambient temperatures (e.g. below 10 °C). In contrast, at higher temperatures (above 30 °C, see also ISO 12884[1]), only PAHs having boiling points above 475 °C (vapour pressure less than 10^{-10} kPa at 25 °C) are determined quantitatively (see Annex F).

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1
blank value solution
solution which contains the chemicals used in making up the sample solution batch and the constituents influencing the measurement in the same or similar concentration as the sample to be analysed, but to which the compound to be determined has expressly not been added

2.2
low-volume sampling device
sampling device with a volume flowrate of 1 m^3/h to 4 m^3/h

2.3
medium/high-volume sampling device
sampling device with a volume flowrate of 10 m^3/h to about 90 m^3/h

3 Symbols and abbreviated terms

3.1 Symbols

A_i peak area of component i

A_{IS} peak area of internal standard

ρ mass concentration

f response factors, slope of straight line

m_i mass of component i

m_{IS} mass of internal standard

M_r relative molecular mass (molecular weight)

V volume

3.2 Abbreviated terms

ASE accelerated solvent extraction

b.p. boiling point

DAD diode array detector (UV absorption)

FLD fluorescence detector

HPLC high performance liquid chromatography

PAH polycyclic aromatic hydrocarbon

SOP standard operating procedure

UV ultraviolet

WHO World Health Organization

4 Principle of the procedure

For sampling, sampling devices with volume flowrates from 1 m^3/h to about 90 m^3/h may be used. The particulate matter, onto which the PAHs are adsorbed, is collected on glass or quartz fibre filters.

The PAHs are extracted and the extract concentrated. If necessary, the extracts may be cleaned by column chromatography using silica gel.

The PAHs are determined by HPLC using DAD or FLD. For quality assurance, internal standards are added.

5 Reagents, apparatus and materials

5.1 Reagents

5.1.1 Solvents for analysis: water, acetonitrile, toluene (all solvents of chromatographic grade).

5.1.2 Solvents for sample preparation: chromatographic grade toluene, cyclohexane and acetonitrile.

The chromatograms of the solvents obtained under the conditions of the illustrative example shall not exhibit any interfering peaks.

5.1.3 Helium, purity 99,999 %; for degasification of solvents.

To avoid interferences, no plastic hoses shall be employed, preferably metal hoses are recommended.

5.1.4 Internal standard

If using DAD: indeno[1,2,3-*cd*]fluoranthene dissolved in toluene, mass concentration e.g. 3 µg/ml (see 6.2). If using FLD: 6-methylchrysene.

5.1.5 Calibration standards

Cyclopenta[*c,d*]pyrene	CPP
Benz[*a*]anthracene	BaA
Chrysene	CHR
Benzo[*b*]fluoranthene	BbF
Benzo[*j*]fluoranthene	BjF
Benzo[*k*]fluoranthene	BkF
Benzo[*a*]pyrene	BaP
Benzo[*e*]pyrene	BeP
Indeno[1,2,3-*cd*]pyrene	INP
Dibenz[*a,h*]anthracene	DBahA
Dibenz[*a,c*]anthracene	DBacA
Benzo[*g,h,i*]perylene	BghiP
Anthanthrene	ANT
Coronene	COR
Dibenzo[*a,l*]pyrene	DBalP
Dibenzo[*a,i*]pyrene	DBaiP
Dibenzo[*a,e*]pyrene	DBaeP
Dibenzo[*a,h*]pyrene	DBahP
Benzo[*a*]chrysene (= picene)	BaC

5.2 Apparatus

5.2.1 Sampling device, consisting of the following parts (commercially available).

5.2.1.1 Sampling head, usually containing the filter.

5.2.1.2 **Pumping system**, e.g. sliding vane-pump or turbine.

5.2.1.3 **Volume meter**, for measuring the sample volume or a flowrate-measuring device.

5.2.1.4 **Electronic or mechanical device**, to establish a constant flow.

5.2.1.5 **Timer**, for selecting the time and duration of the sampling.

5.2.1.6 **Blunt tweezers** (optional), for handling the filters.

5.2.2 Sample preparation equipment

The PAH extraction (see 7.2) is carried out using ordinary laboratory equipment. This may include:

5.2.2.1 **Flasks/reflux condenser**, round-bottomed flask (e.g. 250 ml, or 100 ml if the small filter device is used) with matched reflux condenser and heating bath, or

5.2.2.2 **Ultrasonic bath, beaker**, capacity e.g. 50 ml or 100 ml, or

5.2.2.3 **Soxhlet extractor**, capacity e.g. 30 ml to 50 ml, cellulose extraction thimble, round-bottomed flask (100 ml) with reflux condenser and heating bath, or

5.2.2.4 **ASE apparatus**, device for extracting samples at elevated temperatures and under high pressure.

5.2.2.5 **Vacuum pump**, e.g. a membrane or water-jet pump.

5.2.2.6 **Centrifuge**, with inserts; e.g. of volume 20 ml each.

5.2.2.7 **Chromatography column**, internal diameter e.g. 10 mm, length 230 mm (silica gel column).

5.2.3 Analytical apparatus

5.2.3.1 **High performance liquid chromatograph**, fitted with an isothermal column device, solvent purge system, gradient pump system and a FLD or DAD.

5.2.3.2 **Separation columns**, reverse phase-sorbent columns optimized for PAH analysis (see Annex G).

5.2.3.3 **Recording equipment, work station with screen and printer/plotter** for acquiring, processing, storing and interpreting the data and the possibility of a later baseline correction.

5.2.3.4 **GC microliter syringes**, suitable for metering aliquots.

5.3 Materials

5.3.1 **Collection filter, glass or quartz fibre filters**, collection efficiency better than 99,9 % for particles $< 0{,}5$ µm in diameter, without organic binder, appropriate for the sampling device (circular or square).

NOTE Filters coated or impregnated with polytetrafluoroethene (PTFE) have been used for collection of particle-associated PAHs [2]. Use of these filters, in lieu of those specified, requires validation of their performance by the user.

5.3.2 Sorbent for column chromatography

Silica gel, high purity grade, type 60, particle diameter 70 µm to 200 µm; 15 % mass fraction of water is added 24 h before use. To pack the column, a slurry is formed of 10 g of moistened silica gel in 40 ml of cyclohexane. The slurry, freed from air bubbles by shaking, is packed into the chromatography column. Prior to use, the cyclohexane is drawn off until the level of liquid drops to the surface of the silica gel layer.

6 Measurement procedure

6.1 Sampling

Choose a sampling device appropriate to the measurement task.

Label each collection filter in the laboratory, and, by means of tweezers, place it into the appropriate filter holder. Ensure that the labelling material is not extracted. Fix the filter with a supporting ring. Put the filter holder, with the filter inserted, into a Petri dish and place it in an airtight shipping container (transport box) for transport to the measuring site. At the measuring site, insert the filter holder containing the filter into the sampling head, which is connected to the suction tube, and fix it.

Set the sampling time from 1 h to 24 h, depending on the sampling task. Set the pump and the timer in operation synchronously.

If the flow-controlling device is used in combination with a total volume meter, the sample volume is derived from the volume meter readings at the beginning and the end of the sampling period.

If the flow-controlling device is combined with a flowrate-measuring device, the sample volume is derived from the average flowrate (calculated from the flowrates at the least at the beginning and end of the measurement period) and the elapsed time.

The flowrate-measuring device should also be used to check proper operation of the flow-controlling device at the beginning and end of the sampling period.

Turn the pump off after sampling. Remove the filter holder with the exposed filter from the sampling head. Put the filter holder containing the filter again into a Petri dish and place it in an airtight shipping container (transport box) with the exposed filter side facing upwards for transport. Transport the shipping container (transport box) horizontally. In the laboratory, remove the exposed filter from the filter holder with the aid of tweezers.

Prior to extraction, store the filter in the dark at ambient temperature or below.

At least 10 % of the samples, or a minimum of one per sampling site if fewer than 10 samples are taken at the site, shall be field blanks.

6.2 Sample preparation

Check the purity of the filters and glassware and the purity of the solvents and reagents. For this purpose, add the internal standard solution to an unexposed filter and subject it to the entire analytical procedure (blank value).

The blank values are not taken into account in the calculation, but shall not exceed 10 % of the value of the sample or 10 % of a limit/guide value to be monitored.

Protect the samples and sample solutions against direct light during preparation.

For the extraction, place the filter in a 250 ml round-bottomed flask, cover it with 150 ml of toluene (or 70 ml of toluene in a 100 ml round-bottomed flask if small filters are used) and add then 50 µl of the internal standard solution (see 5.2.2.3). Toluene is especially suitable for the extraction of PAHs[3]. If other solvents (e.g. dichloromethane, acetonitrile) are used, the procedure shall have been validated using NIST standards. Insert the reflux condenser and heat the contents of the flask to boiling for about 20 min. Separate the extract from the filter material and dust particles by filtration.

The extraction may also be performed quantitatively by various other methods:

— in a Soxhlet apparatus (toluene: 8 h, at least 10 cycles per hour);

— in the ultrasonic bath in a beaker (toluene: at least 15 min);

— in an ultrasonic bath followed by centrifugation. The filter is cut into pieces and placed in centrifuge tube, followed by the addition of 15 ml toluene. The tubes are placed in the bath and extracted for 15 min. They are then centrifuged (10 min, 3 000 r/min) and the solvent is decanted. The whole extraction procedure is repeated. Both extraction solvents are combined;

— by accelerated solvent extraction (ASE). The filter is placed in the extraction vessel and extracted at a temperature of 150 °C with toluene.

All methods shall be validated.

Concentrate the toluene solution to few microlitres under reduced pressure (e.g. 13 kPa). Keep this evaporation step under observation at all times.

NOTE If evaporation is continued to dryness and the residue allowed to remain for a time in a vacuum, some PAHs could be lost.

If further clean-up is necessary, add 2 ml of cyclohexane.

Add the cyclohexane solution to the pre-prepared silica gel column (see 5.2.2.7) using a syringe. Rinse the flask then with 2 ml of cyclohexane which is also added with a syringe to the silica gel column. Carry out the elution using 100 ml of cyclohexane. To remove the cyclohexane, concentrate the eluate to a volume of a few milliliters and evaporate it then under a nitrogen stream almost to dryness. Dissolve the residue then in the correct solvent for injection into the HPLC column, e.g. 100 µl of acetonitrile.

NOTE If the origin of the air sample is known and interferents are low, the clean-up using a silica gel column may be unnecessary.

If the extract is not analysed immediately, it shall be stored in a refrigerator. Before analysis, it is allowed to warm to room temperature.

6.3 HPLC analysis

Inject an aliquot of the sample (e.g. 20 µl) into the HPLC apparatus.

An example of operation conditions for HPLC analysis with FLD and DAD in series is given in Annex B.

7 Establishment of the calibration function and verification of the measurement values

7.1 Identification

The separation conditions are optimized with aid of multi-component calibration standard solutions (see 5.1.5), which gives adequate separation of the compounds of interest.

A component in the sample is primarily identified by comparison of its retention time to that of the same substance in the calibration solution analysed under identical conditions. The level of identity shall be reported.

The concentrations of the calibration standards should be in the range of (depending on the measurement task):

— 2 ng/ml to 200 ng/ml, when a FLD is used;

— 20 ng/ml to 1 000 ng/ml, when a DAD is used.