INTERNATIONAL STANDARD

ISO 11338-2

First edition
2003-06-01

Stationary source emissions — Determination of gas and particle-phase polycyclic aromatic hydrocarbons —

Part 2: Sample preparation, clean-up and determination

Émissions de sources fixes — Détermination des hydrocarbures aromatiques polycycliques sous forme gazeuse et particulaire —

Partie 2: Préparation des échantillons, purification et détermination

Reference number
ISO 11338-2:2003(E)

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Published in Switzerland

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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.

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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11338-2 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

ISO 11338 consists of the following parts, under the general title *Stationary source emissions — Determination of gas and particle-phase polycyclic aromatic hydrocarbons*:

— *Part 1: Sampling*

— *Part 2: Sample preparation, clean-up and determination*

Introduction

This part of ISO 11338 describes procedures for sample preparation, clean-up and analysis of polycyclic aromatic hydrocarbons (PAHs) (collected from stack and waste gases), based on either high performance liquid chromatography (HPLC) (see Annexes A and E) or gas chromatography-mass spectrometry (GC-MS) (see Annexes B, C and D).

PAHs are emitted to the atmosphere primarily by the combustion of fossil fuels and wood. PAHs are considered to be an important class of environmental carcinogens. The identification and quantification of PAHs emitted from stationary sources represent a critical aspect in the assessment of air quality.

Stack and waste gases emitted from stationary sources often contain solid particles. Because of the range of their vapour pressures, PAHs are distributed between gas and particle phases. In the atmosphere, PAHs containing four or more rings tend to adsorb onto particles, while PAHs containing two to four rings tend to be present in gaseous form. However in stack and waste gases, the distribution of PAHs between gas and particle phases depends on the temperature, the mass of emitted particles, particle size, humidity, type and concentration of PAH.

During sampling, sample storage and preparation of the sample, losses of PAH can occur and prevent quantitative analysis. These losses can be the result of the volatility of two- and three-ring PAHs, the physical-chemical instability of PAHs in the presence of light, O_3, NO_x, SO_2, HCl and certain heavy metals.

Stationary source emissions — Determination of gas and particle-phase polycyclic aromatic hydrocarbons —

Part 2: Sample preparation, clean-up and determination

1 Scope

This part of ISO 11338 specifies procedures for sample preparation, clean-up and analysis for the determination of gas and particle-phase polycyclic aromatic hydrocarbons (PAH) in stack and waste gases. The analytical methods are capable of detecting sub-microgram concentrations of PAH per cubic metre of sample, depending on the type of PAH and the flue gas volume sampled.

The methods described in this part of ISO 11338 are based on either high performance liquid chromatography (HPLC) or gas chromatography-mass spectrometry (GC-MS).

NOTE ISO 11338-1 describes three methods and specifies minimum requirements for the sampling of PAH in stack and waste gases.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4225:1994, *Air quality — General aspects — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4225 and the following apply.

3.1
polycyclic aromatic hydrocarbon
PAH
compound that contains two or more fused aromatic rings made up of carbon and hydrogen atoms

3.2
stationary source emission
gas emitted by a stationary plant or process and transported to a chimney for dispersion into the atmosphere

3.3
accelerated solvent extractor
ASE
equipment that accelerates the traditional extraction process by using solvent at elevated temperatures

NOTE Pressure is applied to the sample extraction cell to maintain the heated solvent in a liquid state during the extraction.

4 Principle

4.1 Sampling

A representative sample is collected from the gas passing through a duct under isokinetic conditions with the use of a suitable sampling device. The particulate phase is collected on a suitable filter and the gas phase is trapped by condensation onto an adsorbent [e.g. styrene-divinylbenzene polymer resin (XAD-2), polyurethane foam or other adsorbent of comparable efficiency].

4.2 Analysis

After sampling, the sample is removed from the sampling equipment. The parts of the sampling equipment which have been in contact with the sample are washed with solvent. The washings are then combined with the filter(s) and adsorbent and then extracted with a suitable organic solvent, with the use of a Soxhlet extractor [or other validated method, e.g. accelerated solvent extractor (ASE)]. The extract is concentrated by means of a rotary evaporator, followed by further concentration under nitrogen if necessary. Sample clean-up may be necessary before quantification.

An aliquot of the concentrated sample is analysed either by reversed phase high performance liquid chromatography (HPLC) or by gas chromatography-mass-spectrometry (GC-MS). The concentration of each PAH is calculated from the mass of PAH (particle- and gas-phase) determined during analysis and the volume of flue gas sampled corrected to appropriate reference conditions.

5 Safety measures

All PAH should be treated as potential carcinogens. The user should be familiar with the chemical and physical properties of PAH. Measures shall be taken to prevent PAH in solid form, extract or solution coming into contact with the body. PAH can co-distil with the solvent and may cling to the outside of glassware with ground glass stoppers.

Owing in particular to the risks associated with working with PAH in solid form, self-preparation of standard solutions is ill-advised. The use of commercially available standard solutions[1)] minimizes the risk of exposure.

All glassware containing PAH solutions shall therefore be handled with solvent-resistant gloves. Any contamination can be revealed in ultraviolet light by fluorescence. PAH are most dangerous in solid form, becoming electrostatically charged. Therefore PAH should be weighed in a glove box. Unused samples and contaminated equipment, glassware and clothing shall be disposed of properly, taking into account the relevant regulations.

6 Procedures

6.1 HPLC method

6.1.1 General

This subclause describes the preparation, sample clean-up and analytical method for determining the concentration of polycyclic aromatic hydrocarbons (PAH) in stack and waste gases using high pressure liquid chromatography (HPLC).

1) Standard Reference Material (SRM) 1647: Priority Pollutant Polynuclear Aromatic Hydrocarbons, a certified solution of 16 PAH in acetonitrile. This solution is an example of a suitable product available commercially from The National Institute of Standards and Technology (NIST), US Department of Commerce, Gaithersburg, MD, USA. This information is given for the convenience of users of this part of ISO 11338 and does not constitute an endorsement by ISO of this product.

6.1.2 Reagents and materials

6.1.2.1 **Acetonitrile**, HPLC grade.

6.1.2.2 **n-Hexane**, HPLC grade.

6.1.2.3 **Methanol**, HPLC grade.

6.1.2.4 **Pentane**, HPLC grade.

6.1.2.5 **Diethyl ether**, reagent grade, preserved with 2 % ethanol, HPLC grade.

6.1.2.6 **Silica gel**, high purity grade, type 60, 70 mesh to 23 mesh.

6.1.2.7 **Sodium sulfate**, anhydrous, reagent grade, dried by heating at 300 °C for at least 4 h.

6.1.2.8 **Recovery standards for HPLC**: 2-methylchrysene or 6-methylchrysene, purity at least 98 %.

6.1.2.9 **Compressed gases**: high purity helium for degassing the mobile phase and high purity nitrogen for sample concentration.

6.1.2.10 **Aluminium foil**.

6.1.2.11 **Glass wool.**

6.1.3 Apparatus

6.1.3.1 **Soxhlet extractor**, capacity 100 ml to 200 ml, and appropriate condenser.

6.1.3.2 **Glass-fibre filter**, precleaned by heating for 3 h at 200 °C or to an acceptable blank level.

6.1.3.3 **Round-bottom flasks**, capacity 100 ml and either 250 ml or 500 ml depending on the capacity of the Soxhlet extractor.

6.1.3.4 **Rotary evaporator system**, capable of producing a maximum vacuum of 0,1 MPa (1,0 bar), and with a water bath that can be heated to 50 °C.

6.1.3.5 **Kuderna Danish concentrators**, capacity 500 ml, including 10 ml graduated concentrator tubes with ground-glass stoppers, and a 3-ball macro-Snyder column.

6.1.3.6 **Nitrogen evaporative concentrator**: nitrogen blow-down apparatus with flowrate control and temperature-controlled water bath, evaporator tubes of volume 1 ml to 10 ml.

6.1.3.7 **Separation funnels**, of capacity 100 ml and 250 ml.

6.1.3.8 **Glass chromatography column**.

6.1.3.9 **Conical tubes**, of 10 ml capacity.

6.1.3.10 **Extraction thimbles**, pre-extracted with methanol.

6.1.3.11 **Laboratory refrigerator**, capable of cooling to less than 4 °C or **freezer**, capable of cooling to less than −15 °C.

6.1.3.12 **Bumping granules**, solvent extract.

6.1.3.13 **Oven**, capable of maintaining 500 °C.

6.1.3.14 High Performance Liquid Chromatography (HPLC) system, consisting of constant-flow pumps adjusted with gradient controller, an injector capable of injecting sample volumes up to 20 µl, a means of controlling the column temperature within the range 29 °C to 40 °C ± 1 °C, a fluorescence detector with programmable excitation and emission wavelengths and a UV detector adjusted to a wavelength of 229 nm, and accessories including column supplies, recorders and gases.

6.1.3.15 HPLC separation column, of glass or stainless steel [20 mm to 250 mm long and 3 mm to 4,6 mm internal diameter (ID)], based on silica, derivatized with C18 alkyl chains, of particle size 3 µm to 5 µm.

6.1.3.16 HPLC guard column, stainless steel column for use in reversed phase chromatography (10 mm long by 2 mm ID, screen mesh < 1 µm, frit 0,5 µm) or other suitable columns**.**

Guard columns should always be used, because sample and eluent contamination can result in excessive column pressures leading to altered selectivity.

6.1.3.17 Degassing system for HPLC, helium

Eluents should be degassed to avoid quenching of the fluorescence signal.

6.1.3.18 Filtration system, including filter of pore size 45 µm for filtration of mobile phase.

6.1.3.19 Syringes, 10 µl, 25 µl, 50 µl, 100 µl, 250 µl, 500 µl and 1 000 µl for preparing calibration, reference standard and spiking solutions.

6.1.4 Sample preparation

6.1.4.1 Storage conditions of samples

Owing to possible reactions of PAH with light and components present in air, all sampling parts containing PAH should be stored until required for laboratory preparation, in sealed containers protected from light and at temperatures either between 0 °C to 4 °C or below −15 °C. Samples stored between 0 °C to 4 °C shall be extracted within one week after sampling has been completed. If samples are stored at a temperature of −15 °C or below, extraction shall take place within one month. Any condensate shall be acidified with hydrochloric acid to pH ≈ 2, and may then be stored for up to 14 days.

6.1.4.2 Extraction of filters and solid sorbents

Remove the filter and solid sorbents from their sealed containers and place in the pre-extracted Soxhlet thimble. Immediately prior to extraction add 500 µl of the recovery standard, 2- or 6-methylchrysene (6.1.2.8) in acetonitrile (mass concentration of ≈ 1 µg/ml), to the sorbent or filter in order to determine the recovery of the extraction procedure. If separate analyses of the sorbent and filter are required, both shall be spiked.

Carry out the extraction with 10 % diethyl ether (6.1.2.5) in n-hexane (6.1.2.2) for approximately 20 h, at a reflux rate of 4 cycles per hour.

Add the recovery standard to all related samples, including field and method blanks.

Alternatively, other extraction techniques (e.g. ASE) or other solvents or solvent mixtures may be used if validated by the user.

6.1.4.3 Extraction of condensate

Transfer the condensate into the separation funnel. Rinse the impingers or condensate flasks with n-hexane (6.1.2.2) and transfer the n-hexane to the separation funnel. Shake for at least 5 min. Allow to settle and then separate the n-hexane from the condensate. Carry out a further extraction on the condensate under the same conditions and combine the n-hexane fractions. Dry the combined n-hexane fractions over sodium sulfate (6.1.2.7).

The volume of n-hexane used in each of the two extractions shall be at least 20 % of the volume of the condensate.

6.1.4.4 Concentration of the extract

Combine the dried n-hexane extracts of the condensate with the extract of the filter and solid sorbent. Filter the combined extracts over a pre-cleaned glass-fibre filter (6.1.3.2) and transfer to the rotary evaporator. Concentrate the extract to a volume of approximately 2 ml. Transfer the extract quantitatively with n-hexane to a calibrated 10 ml conical tube. Add 1 ml of acetonitrile (6.1.2.1) to the tube. Then place the tube in a water bath at 25 °C and concentrate the extract under a gentle stream of nitrogen until the hexane (upper layer) and a small part of the acetonitrile is evaporated. Adjust the volume of the concentrated sample extracts to 1,0 ml with acetonitrile.

Mix the sample well and transfer to sealed brown vials for storage at less than 4 °C, protected from light, until analysed. Concentrated extracts should be analysed within 30 days.

A rotary evaporator (6.1.3.4) may be used with a vacuum of approximately 0,1 MPa pressure and a water bath at a temperature not exceeding 45 °C. If validated by the user, other evaporation systems may be used to concentrate the extract. If the extract is concentrated to dryness, substantial losses of PAH may occur; therefore the sample should be discarded where this has occurred.

Other evaporation systems to concentrate the extract may be used if validated by the user.

NOTE 1 Concentrating the sample extract to a volume of 1 ml may not be needed, depending on the target detection limits, the sensitivity of the detector and the flue gas volume sampled.

NOTE 2 The last evaporation step with the use of nitrogen is the most critical aspect in sample preparation. Losses of volatile PAH due to the final concentration step of sample extracts can lead to losses up to 10 % for 2- to 4-ring PAH if n-hexane is the extraction solvent. If toluene is used as extraction solvent, losses up to 10 % to 40 % for 2- to 4-ring PAH can be expected.

6.1.4.5 Sample clean-up

6.1.4.5.1 General

Clean-up procedures may not be necessary for relative clean matrices. Complex matrices require a purification stage, to eliminate interferences caused by the presence of polar and non-polar compounds.

If dichloromethane is used for extraction of the sample, it should be solvent-exchanged with n-hexane prior to the clean-up procedure.

6.1.4.5.2 Column preparation

Extract silica gel, type 60, in a Soxhlet extractor with dichloromethane for 6 h (minimum rate, 3 cycles/h) and then activate by heating in a foil-covered glass container for 16 h at 450 °C.

Pack a small piece of glass wool into the bottom of a glass chromatography column of 15 ml to 25 ml capacity (e.g. 160 mm long × 11,5 mm ID). Slurry 10 g of the activated silica gel with pentane and pour into the column. Tap the column gently as the slurry is settling to assure proper packing. Finally, add 1 g of anhydrous sodium sulfate to the top of the silica gel.

6.1.4.5.3 Column chromatography

Prior to use, pre-elute the column with 40 ml of pentane and discard the eluate. While the pentane pre-eluent still covers the top of the column, quantitatively transfer 1 ml of sample extract in n-hexane to the column, and wash on with a further 2 ml of n-hexane to complete the transfer. Allow to elute through the column. Immediately prior to exposure of the sodium sulfate layer to the air, add 25 ml of pentane and continue elution. The pentane eluate may be discarded.

Finally, elute the column with 25 ml of dichloromethane in pentane (4:6 volume ratio) at 2 ml/min and collect in a 100 ml round-bottomed flask (6.1.3.3). Further concentrate the extract to a volume of ~2 ml to 5 ml. Transfer the extract quantitatively to a 10 ml conical tube (6.1.3.9). Transfer the tube to a water bath at 25 °C and concentrate the extract to near dryness under a gentle stream of nitrogen. Then solvent-exchange the sample extracts with acetonitrile and adjust the volume to 1,0 ml.

Clean-up columns are commercially available and may be used, if validated.

NOTE 1 The pentane fraction contains the aliphatic hydrocarbons. If required, this fraction can be analysed for specific aliphatic hydrocarbons.

NOTE 2 An additional elution of the column with 25 ml of methanol will elute polar compounds (e.g. oxygenated, nitrated and sulfonated PAH).

6.1.5 Sample analysis

6.1.5.1 Instrumentation

HPLC analysis is performed on an analytical system consisting of constant-flow pumps adjusted with a gradient controller, injector, column heater, fluorescence detector with programmable excitation and emission wavelengths, and a UV detector adjusted to a wavelength of 229 nm.

Typical instrument parameters are:

— Column: glass or stainless steel, 200 mm long, 4,6 mm ID;

— Stationary phase: silica derivatized with C18 alkyl chains, particle size 5 µm;

— Mobile phase: solvent A acetonitrile/water (50 % volume fraction)
solvent B acetonitrile (100 % volume fraction)
linear gradient, with respect to time, changing from 100 % solvent A to 100 % solvent B;

— Flowrate: 0,8 ml/min;

— Injection volume: 20 µl;

— Column temperature: (29 ± 1) °C.

A fluorescence detector with programmable wavelengths should be used for more selectivity in complex matrices. The excitation and emission wavelength combinations can be optimized for each component. An example is given in Annex A. Acenaphthylene is determined by UV (at 229 nm) because this component does not exhibit fluorescence.

A minimum column length of 20 cm is desirable for sufficient peak separation. In order to achieve proper results, injection volumes of 100 µl or more, column lengths of 15 cm or less and gradients of 25 min or less should be avoided. Typical gradient time is about 40 min to 60 min.

NOTE 1 Choice of mobile phase, injection volume and flowrate depends on manufacturer's column specifications.

NOTE 2 Diode-array detectors provide an opportunity to improve selectivity by using the entire UV spectrum of a compound in order to identify false positives.

6.1.5.2 Instrument calibration

Prepare calibration standards of individual PAH at a minimum of five concentration levels by adding appropriate volumes of stock standards to a volumetric flask. The lowest concentration shall be at a level near the quantification limit.