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Karakterizacija odpadkov – Določevanje policikličnih aromatskih ogljikovodikov (PAH) v odpadkih z uporabo plinske kromatografije z masno spektrometrijsko detekcijo (GC-MS)

Characterization of waste - Determination of polycyclic aromatic hydrocarbons (PAH) in waste using gas chromatography mass spectrometry (GC/MS)

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Characterization of waste - Determination of polycyclic aromatic hydrocarbons (PAH) in waste using gas chromatography mass spectrometry (GC/MS)

Caractérisation des déchets - Dosage des hydrocarbures aromatiques polycycliques (HAP) dans les déchets par chromatographie en phase gazeuse/spectrométrie de masse (CG/SM)

Charakterisierung von Abfällen - Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK) in Abfall mittels Gaschromatographie-Massenspektrometrie (GC/MS)

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Foreword

This document (prEN 15527:2006) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, the secretariat of which is held by NEN.

This document is currently submitted to the CEN Enquiry.

Introduction

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous because of the fact that they are released in appreciable quantities every year into the environment through the combustion of organic matters such as coal, fuel oils, petrol, wood, refuse and plant materials. Since some of these PAH compounds are carcinogenic or mutagenic, their presence in the environment (air, water, soil, sediment and waste) are regularly monitored and controlled. At present determination of PAH are carried out in these matrices in most of the routine laboratories following the preceding steps for sampling, pre-treatment, extraction, clean up by measurement of specific PAH by means of Gas chromatography in combination with mass spectrometric detection(GC-MS) or by HPLC in combination with UV-DAD- or Fluorescence-detection (HPLC-UV-DAD/FLD). However, the different matrices covered in this standard may contain a lot of contaminants. For this reason, the GC-MS method seems to be most appropriate for waste analysis.

1 Scope

This document specifies the quantitative determination of 16 polynuclear aromatic hydrocarbons (PAH) according to the priority list of the Environmental Protection Agency (EPA, 1982). This document is applicable for wastes such as contaminated soil, sludge and rubble, bitumen or waste containing bitumen.

This document describes a gas chromatographic method with mass spectrometric detection (GC-MS). Under the conditions specified in this document, a lower limit of application of 0,01 mg/kg (for each individual PAH) and 0,1 mg/kg (sum of 16 PAH) can be ensured (expressed as dry matter).

NOTE With this method also other PAH compounds can be analysed providing suitability is proven.

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.

prEN 14346, *Characterization of waste — Calculation of dry matter by determination of dry residue and water content*

EN 15002, *Characterization of waste — Preparation of test portions from the laboratory sample*

ISO 14507, *Soil quality — Pretreatment of samples for determination of organic contaminants*

3 Terms and definitions

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

3.1
analyte
selected polycyclic aromatic hydrocarbons (PAH) with 2 to 6 condensed aromatic rings (see table 1)

3.2
calibration standard
solution of PAH prepared from a secondary standard and/or stock solutions of native PAH and deuterated PAH used to calibrate the response of the instrument

3.3
extraction standard
deuterated PAH of medium volatility added to the sample before extraction and used for control of the extraction efficiency

3.4
internal standard
deuterated PAH added to the sample after extraction and used for quantification of the concentrations of PAH in the sample

3.5
injection standard
deuterated or unlabeled PAH that are unlikely to be present in waste samples added to the sample extract before injection into the GC, to monitor the recovery of the internal standards

4 Principle

The PAH are extracted from the sample by use of acetone and hexane-like solvents. If appropriate, the extract is purified by column chromatography.

The extract is analysed by GC-MS using a capillary column with an immobile phase of low polarity. PAH are identified with GC-MS. PAH are quantified using an internal-standard-method.

5 Reagents

5.1 General

All reagents shall be of recognised analytical grade. The suitability of the reagents shall be checked by running a blank determination as described in 11.1.

5.2 Reagents for extraction procedures

5.2.1 Reagents for extraction by shaking/sonification

5.2.1.1 Acetone

5.2.1.2 Petroleum ether (Boiling range 40 °C to 60 °C) or n-hexane or iso-hexane or cyclohexane

5.2.1.3 Sodium chloride, anhydrous

5.2.1.4 Distilled water or water of equivalent quality

5.2.1.5 Anhydrous sodium sulphate

Heated for at least 6 h to 550 °C ± 20 °C, cooled to about 200 °C in the furnace and then to ambient temperature in a desiccator containing magnesium perchlorate or a suitable alternative. The anhydrous sodium sulphate shall be kept carefully sealed.

5.2.2 Reagents for Soxhlet extraction

5.2.2.1 mixture of acetone and petroleum ether (boiling range 40 °C to 60 °C) or n-hexane or iso-hexane or cyclohexane 1:1 (*v/v*)

5.3 Reagents for clean-up procedures

5.3.1 Clean-up A – Aluminium oxide

5.3.1.1 Aluminium oxide Basic or neutral, specific surface 200 m^2/g, activity Super I

5.3.1.2 Deactivated aluminium oxide. Add 10 g of water to 90 g of aluminium oxide (5.3.1.1). Shake until all lumps have disappeared. Allow the aluminium oxide to condition before use for some 16 h, sealed from the air.

5.3.2 Clean up B- Silica gel 60 for column chromatography

5.3.2.1 Silica gel 60, particle size 63 µm to 200 µm

5.3.2.2 Silica gel 60, water content: mass fraction $w(H_2O)$ = 10 %. Silica gel 60, heated for at least 3 h at 450 °C, cooled down in a desiccator and stored containing magnesium perchlorate or a suitable drying agent. Before use heat at least for 5 h at 130 °C in a drying oven. Then allow to cool in a desiccator and add 10 % water *(w/w)* in a flask. Shake for 5 min intensively by hand until all lumps have disappeared and then for 2 h in a shaking machine. Store the deactivated silica gel in the absence of air, use it for maximum of one week.

5.4 Reagents for gas chromatographic analysis

5.4.1 Carrier gas for gas chromatography - MS, helium or hydrogen of suitable purity

5.5 Standards

5.5.1 Calibration standards, extraction standards and internal standards

Choose the internal standards substances whose physical and chemical properties (such as extraction behaviour, retention time) are similar to those of the compounds to be analysed. Deuterated PAH should be used as internal standards for the GC-MS method for evaluation of results. Verify the stability of the internal standards regularly. Table 1 contains native and a minimum number of deuterated PAH to be used for calibration of specific analyte. The use of isotope dilution (each native PAH is quantified with respect to his labelled analogue) is recommended.

NOTE Certified solutions of PAH, and single solid PAH substances with certified purity are available.

Table 1 — Native PAH and deuterated PAH

PAH reference substances		Internal standard substances: (deuterated PAH)
Naphthalene	(CAS No. 91-20-3)	Naphthalene- D_8
Acenaphthene	(CAS No.83-32-9)	Acenaphthene-D_{10}
Acenaphthylene	(CAS No.208-96-8)	
Fluorene	(CAS No.86-73-7)	
Anthracene	(CAS No.120-12-7)	
Phenanthrene	(CAS No. 85-01-8)	Phenanthrene-D_{10} (extraction standard)
Fluoranthene	(CAS No.206-44-0)	
Pyrene	(CAS No.129-00-0)	
Benz(a)anthracene	(CAS No.56-55-3)	Benz(a)anthracene-D_{12}
Chrysene	(CAS.No.218-01-9)	
Benzo(b)fluoranthene	(CAS No. 205-99-2)	
Benzo(k)fluoranthene	(CAS No.207-08-9)	
Benzo(a)pyrene	(CAS No.50-32-8)	Benzo(a)pyrene-D_{12}
Indeno(1,2,3-cd)pyrene	(CAS No.193-39-5)	
Dibenz(ah)anthracene	(CAS No.53-70-3)	
Benzo(ghi)perylene	(CAS No.191-24-2)	
		Perylene-D_{12}

5.5.2 Injection standards

A deuterated PAH is added to the final extract before GC-MS injection to check the recovery of the deuterated internal standards. Suitable injection standards are D_{10}-1-methylnaphthalene, D_{10}-benzo(e)pyrene and D_{12}—triphenylene.

6 Apparatus

6.1 Extraction and clean-up procedures

Customary laboratory glassware. All glassware and material that comes into contact with the sample or extract shall be thoroughly cleaned.

6.1.1 Extraction procedures

6.1.1.1 Glass sample bottles of appropriate size with glass stopper or screw top and polytetrafluorethene seal (PTFE).

6.1.1.2 Shaking device, with horizontal movement (200 to 300 strokes per minute).

6.1.1.3 Ultrasonic bath

6.1.1.4 Water bath, adjustable up to 100 °C.

6.1.1.5 Separatory funnels with a capacity of 1 l.

6.1.1.6 Conical flasks with a capacity of 500 ml.

6.1.1.7 Soxhlet extraction apparatus, consisting of: round bottom flask e. g.100 ml, Soxhlet extractors and soxhlet thimbles e. g. 27*100 mm, vertical condensers e. g. 300 mm, water-bath or heating mantle as heating apparatus.

6.1.1.8 Evaporator, Kuderna Danish or other evaporators, e. g. a rotary evaporator, if found to be equally suitable.

6.1.2 Clean-up procedures

6.1.2.1 Quartz wool or silanized glass wool

NOTE Working with quartz wool imposes a risk to health through the release of fine quartz particles. Inhalation of these should be prevented by using a fume cupboard and wearing a dust mask.

6.1.2.2 Boiling chips glass or porcelain beads.

6.1.2.3 Calibrated test tubes with a capacity of 10 ml to 15 ml and ground glass stopper.

6.1.2.4 Chromatography tubes, Chromatography column of glass, 5 mm to 10 mm internal diameter, length e. g. 600 mm.

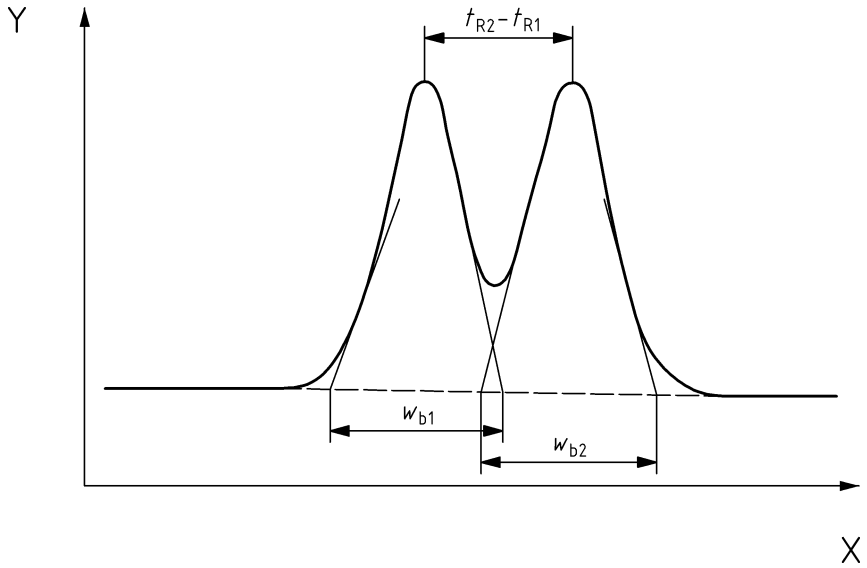
6.2 Gas chromatograph

Gas chromatograph equipped with an on-column, split/splitless or programmable temperature vaporizer (PTV) injection system, capillary column (6.3) and a mass spectrometric detector (GC-MS).

6.3 Capillary columns

Each comprising a 5% phenyl-methyl silicone stationary phase coated onto fused silica capillary column or an equivalent chemically bonded phase column. The dimensions should be sufficient to separate the critical pairs mentioned below (e.g. column length of 50 m, internal diameter of 0,25 mm and film thickness of 0,2 µm).

Sufficient resolution between the chromatographic peaks of critical pairs benzo(b)fluoranthene / benzo(k)fluoranthene as well as of benzo(a)pyrene / benzo(e)pyrene is to be set as quality criteria for the capillary column. The resolution is defined according to figure (1) and equation (1):



Key
X Time
Y Intensity

Figure 1 — Resolution of chromatographic peaks

$$R = 2\frac{(t_{R2} - t_{R1})}{w_{b1} + w_{b2}} \quad (1)$$

Where:

R is the resolution;

t_{R1}, t_{R2} are the retention times of each eluted component 1 and 2;

w_{b1}, w_{b2} are the peak widths of each peak at its base.

The resolution should be better than 0,5 for the benzo(b)fluoranthene/benzo(k)fluoranthene critical pair. The separation should be complete for the benzo(a)pyrene/benzo(e)pyrene critical pair.

6.4 Preparation of standard solutions

6.4.1 General

Because of the toxicity of the PAH, commercially available - preferably certified - standard solutions should be used. Avoid skin contact.

6.4.2 Single substance stock solution

Solutions of the individual substances of native and deuterated PAH (see table 1) in a non-polar solvent with a mass concentration of e. g. 10 µg/ml. The solutions can be prepared from pure solid PAH or purchased as solution. These solutions are used for confirmation and identification of single PAH in the chromatogram. The single substance stock solutions are to be stored in a dark place at about 4 °C. Store the diluted standard solutions at about 4 °C protected from light and evaporation. They are stable for about 1 year.

6.4.3 Multiple substance stock solution of native PAH

Dilute the solution of the native PAH in a non-polar solvent to a mass concentration of e. g. 10 µg/ml for each individual PAH.

6.4.4 Multiple substance stock solution of deuterated PAH

Multiple deuterated PAH standards for use as internal standard are commercially available as mixtures in a suitable solvent or can be prepared from pure solid PAH. The solutions can be diluted to the same mass concentration of e. g. 10 µg/ml for each individual deuterated standard.

NOTE The standard solutions should be in the same solvent as the extract.

6.4.5 Calibration standard solutions

Prepare a series of calibration standard solutions(at least 5) covering a suitable range of concentrations by transferring different volumes of the multiple substance stock solution of native PAH standards (6.4.3) and a constant volume of the internal standard solution (6.4.4) and injection standard solution into a volumetric flask and fill up to the mark with non-polar solvent. Transfer for example 500 µl of both multiple stock solutions of native and deuterated PAH into a volumetric 5 ml flask and fill up to the mark with cyclohexane. 1 µl of this calibration solution contains 1 ng of the respective individual native and deuterated substances.

NOTE Concentration of internal standards in the sample extract should ideally be of the same magnitude as that of the analyte (e. g. 1 µg/ml).

6.4.6 Preparation of extraction standard solution

Prepare a stock solution of deuterated PAH (e. g. Phenanthrene-D_{10}) according to 6.4.2 in a non-polar solvent. The amount of the extraction standard has to be adjusted so that the concentration in the final extract for GC-MS is the same as that in the calibration solutions.

6.4.7 Preparation of internal standard solution

Multiple substance stock solution of deuterated PAH (6.4.4) are used for spiking to the sample after extraction. The amount of the internal standards has to be adjusted so that their concentration in the final extract for GC-MS is the same as that in the calibration solutions.

6.4.8 Preparation of injection standard

This is needed to check the recovery of the deuterated internal standards. A single substance stock solution (6.4.2) e. g. deuterated benzo(e)pyrene or other PAH which is not interfering with the target analyte can be used.

A deuterated PAH not mentioned in the scope is added before injection into the GC, to monitor variability of the instrument response, the so called injection standard. The recovery of the internal standards throughout the whole method can be calculated on the basis of the response of the internal standard relative to the injection standard.

7 Hazards

Anyone dealing with waste and sludge analysis has to be aware of the typical risks of that kind of material irrespective of the parameter to be determined. Waste and sludge samples may contain hazardous (e. g. toxic, reactive, flammable, infectious) substances, which can be liable to biological and/or chemical reaction. Consequently it is recommended that these samples should be handled with special care. The gases which may be produced by microbiological or chemical activity are potentially flammable and will pressurise sealed

bottles. Bursting bottles are likely to result in hazardous shrapnel, dust and/or aerosol. National regulations should be followed with respect to all hazards associated with this method.

Certain PAH are carcinogenic and must be handled with extreme care. Skin contact with solid materials, PAH standard solutions and sample extracts must prevented. PAH may co-evaporate with solvents and deposit on the outer walls of stoppered glass bottles and containers. Hence, all containers containing solutions of PAH in organic solvents or sample extracts must be handled wearing solvent resistant disposable protecting gloves. PAH contamination of containers may be detected by irradiation with 366 nm U.V. light. Vessels containing PAH solutions should be stored in beakers to absorb any spillage in case of breakage. There is a particular risk by inhalation of PAH dust when working with crystalline PAH standards. Thus, these materials must only be handled where proper facilities are available (e. g. adequate fume hoods, protective clothing, dust masks etc). Solvent solutions containing PAH must be disposed of in a manner approved for disposal of toxic wastes.

NOTE Preferably, certified reference standard solutions of suppliers specialised in their preparation should be used.

8 Interference

8.1 Interference during sampling, storage and extraction

Use sampling containers of materials (preferably of steel or glass) that do not change the sample during the contact time. Avoid plastics and other organic materials during sampling, sample storage or extraction. Keep the samples from direct sunlight and prolonged exposure to light.

During storage of the samples, losses of PAH may occur due to adsorption on the walls of the containers. The extent of the losses depends on the storage time.

8.2 Interference due to co-elution

There is a certain risk of co-elution of target PAH in one peak with other PAH not mentioned in the scope which can interfere with quantification. These interferences may lead to unresolved or incompletely resolved peaks and, depending on their magnitude, affect accuracy and precision of the analytical results.

Chromatographic separation of dibenzo(ah)anthracene and indeno(1,2,3-cd)pyrene can be critical under certain circumstances. But due to their differences in molecular masses, they can be quantified accurately.

Sufficient chromatographic resolution of the GC peaks for benzo(a)pyrene and benzo(e)pyrene as well as for benzo(b)fluoranthene and benzo(k)fluoranthene allowing accurate quantification of these compounds can be achieved by selecting an appropriate chromatographic column, which meets the performance criteria for separation of these critical pairs.

On most capillary columns benzo[j]fluoranthene (B[j]F) co-elutes with either benzo[b]fluoranthene (B[b]F) or benzo[k]fluoranthene (B[k]F) in one peak. Hence, measured concentrations of the target compounds B[b]F and B[k]F usually represent the sum of B[b]F and B[j]F and B[k]F and B[j]F, respectively. This co-elution shall be checked for by analysing mixtures of B[j]F / B[b]F and B[j]F / B[k]F and indicated when reporting results. The contribution of B[j]F to the signal assigned to B[b]F and B[k]F, respectively, can neither be neglected nor estimated reliably.

9 Sample conservation

In principle, the samples shall be analysed as soon as possible after sampling. This applies in particular to the examination of microbiologically active solids. Field moist samples can be stored at a temperature of (4 ± 2) °C in sample containers in a dark place for a maximum of one week. If the sample cannot be processed within a week, it has to be stored at temperatures below –18 °C. In order to prevent the degradation of the analytes, dried samples must be stored in the dark preferably at a temperature of about 4 °C.