# HJ

STANDARD OF THE ENVIRONMENTAL

PROTECTION AUTHORITY

## HJ/T 40-1999

# Stationary Source Emission – Determination of Benzo (a) Pyrene – High Performance Liquid Chromatography

固定污染源排气中苯并(a)芘的测定 高效液相色谱法

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# Stationary Source Emission – Determination of Benzo (a) Pyrene – High Performance Liquid Chromatography

## 1 Scope

**1.1** This Standard is applicable to the determination of benzo (a) pyrene discharged from a stationary pollution source in an intentional emission manner.

**1.2** When the gas production volume is 1.0$m^3$, the constant volume of the sample is 1.0mL, and chromatographic injection volume is 10μL, the limit of detection for the benzo (a) pyrene shall be 2ng/$m^3$, and the concentration range for quantitative determination shall be 7.6ng/$m^3$~4.0μg/$m^3$.

## 2 Method Principle

Collect samples by non-glue glass fiber filter cartridge or glass fiber filter membrane; extract benzo (a) pyrene by cyclohexane; and pass the extract through a Florisil chromatography column; then use a mixed solvent of dichloromethane and acetone to elute the benzo (a) pyrene absorbed on the column; after concentration, then measured on a high performance liquid chromatograph that is equipped with a fluorescence detector.

## 3 Normative References

The following standards contain provisions which, through reference in this Standard, constitute provisions of this Standard.

GB 16157-1996 The Determination of Particulates and Sampling Methods of Gaseous Pollutants Emitted from Exhaust Gas of Stationary Source

## 4 Reagents and Materials

Unless otherwise specified, analytical reagents and pure water prepared in accordance with 4.1, both of which comply with the national standard, are used in the analysis.

**4.1** Pure water

Use deionized water (or distilled water) to add potassium permanganate; and re-distill by an all-glass distiller under alkaline conditions. During the whole distillation process, the purple-red color shall always be maintained; otherwise, potassium permanganate shall be added. The obtained pure water shall have no significant interference peak after the blank test of this method.

**4.2** Methanol

Use an all-glass distiller to add alkali for re-distilling; collect the distillate; filter it through 0.45μm microporous filter membrane and use it. There shall be no significant interference peak after the blank test of this method.

**4.3** Methylene chloride

Use an all-glass distiller to add alkali for re-distilling; there shall be no significant interference peak after the blank test of this method.

**4.4** Acetone

Undertake the treatment with the same procedures as 4.3.

**4.5** Cyclohexane

Undertake the treatment with the same procedures as 4.3.

**4.6** Florisil: 60~100mesh, it is used for chromatographic analysis.

Heat for 2h at 400°C; after cooling, use water (4.1) to adjust evenly till the water content is 11%; seal to store into the reagent bottle with grinding mouth.

**4.7** Benzo (a) pyrene standard stock solution

Accurately take 20.0 mg of solid benzo (a) pyrene standard substance; dissolve it in 60mL of cyclohexane (4.5); transfer to a 100 mL volumetric flask; and dilute to the mark with cyclohexane (4.5). Or use benzo (a) pyrene standard solution and dilute it with cyclohexane (4.5) or methylene chloride (4.3) to the concentration of 200μg/mL.

The above stock solution shall be stored in a refrigerator at 3~5°C.

**4.8** Benzo (a) pyrene standard use solution

Pipette 1.00mL of standard stock solution (4.7) into a 100mL volumetric flask; and dilute to the mark with cyclohexane (4.5) or methylene chloride (4.3). As the sensitivity of the used instrument or the concentration of the analyzed sample is different, the concentration of the standard use solution shall be changed as needed.

Select the sampling method according to 8.2 in GB 16157-1996 (the selected sampling method shall be consistent with the configuration of the sampling instrument); install the glass fiber filter cartridge or filter membrane on the sampler; and take sampling according to certain items (depending on the sampling method) in 8.3~8.6; and the gas production volume is about 1.0$m^3$.

**6.3** Sample storage

The collected samples must be protected from light, or they may be wrapped in black paper and stored in a 3~5°C freezer. Pre-processing shall be carried out within 24 hours as soon as possible after sampling; and the processed samples shall finish the analysis within 1 month.

# 7 Pre-Processing of Sample

**7.1** Extraction of benzo (a) pyrene in the sample: carefully put the non-glue filter cartridge or ultrafine glass fiber filter membrane (after folding the dust side inward) of the sampled product into the extraction cylinder (be careful not to block the siphon return pipe) of the Soxhlet extractor (5.3). Add 80mL of cyclohexane (4.5); place it in a water bath (5.9) at a temperature above 95°C; continue to reflux for extraction for 6h; and cool for later use.

**7.2** Purification of the extract: The obtained extract (7.1) is purified (and enriched) by a Florisil chromatography column.

**7.2.1** Filling of the chromatography column: first fill a small amount of glass wool (5.7) into the lower end of the glass chromatography column (5.4) to support the filler. Add 2~3mL of cyclohexane (4.5) to wet the column. Weigh about 5g of Ferolisil (4.6) in a small beaker; make a homogenate with cyclohexane (4.5); fill the above column by wet filling method; and release excessive cyclohexane in the column to above the interface of the filler.

**7.2.2** Purification of the extract: add the sample extract (7.1) from the top of the chromatography column (7.2.1); and use 20~40mL cyclohexane (4.5) to clean the Soxhlet extractor used in the Subclause (7.1) for three times; then it is added to the upper end of the column at the same time; and the entire solution passes through the column at a flow rate of <4mL/min; and the cyclohexane passing through the column is recovered. Then use 20mL of a mixed solution of methylene chloride (4.3) and acetone (4.4) ($CH_2Cl_2$ : $CH_3COCH_3$ = 4 : 1) to elute the benzo(a) pyrene adsorbed on the column. The eluent was collected in 25mL K-D concentrating bottle (5.5) to be concentrated. (If the content of benzo (a) pyrene in the sample is high, it does not need to be concentrated, and the liquid chromatograph can be used for analysis after making constant volume).

**7.3** Concentration of the sample: connect the K-D concentrating bottle containing the

**8.2.6.2** Paper speed: 0.3 or 0.5 cm/min.

**8.3** Calibration

**8.3.1** Quantification by external standard method

**8.3.2** Standard sample

**8.3.2.1** For the preparation of standard samples, see Subclause 4.8.

**8.3.2.2** Use frequency: use standard samples (4.8) to perform periodic re-calibration. Depending on the stability of the chromatograph, determine the length of the re-calibration cycle. Generally, it is measured 1 or 2 times every working day, or calibrate once after measuring every 5 samples.

**8.3.2.3** Conditions for using standard samples in chromatographic analysis

**8.3.2.3.1** The injection volume of the standard sample and the specimen shall be the same, and the response value shall be similar.

**8.3.2.3.2** Adjust the repeatability condition of the instrument: under the condition of normal operation of the instrument, continuously feed 10μL of the standard sample twice; and if the relative deviation of its response value (peak height or peak area) is no greater than 5%, then the instrument is considered to be in stable state.

**8.3.3** Representation of calibration data: draw the calibration curve by using the response value against the injection volume; then obtain a straight line passing through the origin. The ratio of the response value to the injection volume is a constant; and the average ratio or response factor may be used to replace the calibration curve to calculate the measurement result.

**8.4** Determination

**8.4.1** Injection

**8.4.1.1** Injection method: injection by the automatic sampler; or injection by manual six-way valve using a syringe.

**8.4.1.2** For sample injection volume, see Subclause 8.2.5. The automatic sampler may be preset on the instrument panel when injecting samples.

**8.4.2** Record

**8.4.2.1** Write down the magnification (or attenuation) multiples on the recording paper (or integrator) and the chart drive speed of the recording paper.

**8.4.2.2** For the chromatographic peak of benzo (a) pyrene, it may be checked by a standard sample; and the retention time of the corresponding peak may be recorded.

Calculate the "emission rate" of intentional emission of benzo (a) pyrene according to 11.4 in GB 16157-1996, which is expressed by (kg/h).

## 10 Precision and Accuracy

**10.1** Precision: Two laboratories analyzed a uniform sample with a benzo (a) pyrene content of 0.707mg/L. The results are:

The repeatability standard deviation is 0.0064; the repeatability relative standard deviation is 0.91%; and the repeatability is 0.029.

The reproducibility standard deviation is 0.011; the reproducibility relative standard deviation is 1.6%; and the reproducibility is 0.032.

**10.2** Accuracy: two laboratories perform six spike recovery tests on uniform samples without pre-processing; and the obtained spike recovery rate is between 96.9% ~ 101%; with an average of 98.5%. For the actual samples, six throughout spike recovery tests are performed, and the obtained spike recovery rate is between 71.3% ~ 91.3%, with an average of 82.8%.

## 11 Description

**11.1** Since benzo (a) pyrene is one of the most dangerous and strong carcinogens in polycyclic aromatic hydrocarbons, extreme care must be taken during operating. The human body is not allowed to come into contact with benzo (a) pyrene (including polycyclic aromatic hydrocarbons) solid substances, solvent extracts and standard products. Benzo (a) pyrene (polycyclic aromatic hydrocarbon) may volatilize along with the solvent and adhere to the outside of the bottle with stopper; so, the solvent-resistant gloves must be used to handle the relevant container and the experimental operation process. The container that is contaminated by the benzo (a) pyrene (polycyclic aromatic hydrocarbons) may be inspected under 364 nm ultraviolet radiation by an ultraviolet lamp; and immersed in chromic acid lotion for 4h. The standard solution shall be prepared in a laboratory with appropriate equipment (such as suitable poison gas cabinets, protective clothing, dust masks, etc.). For the preparation of standard solutions with solid benzo (a) pyrene, it cannot be carried out without proper safety equipment and the use technology has not been accurately mastered.

**11.2** The methanol, cyclohexane, methylene chloride and acetone that are used in this experiment are all flammable organic solvents and shall be operated in a fume hood.

**11.3** This experiment shall be carried out without direct sunlight.

**11.4** The experimental waste liquid shall not be discarded at will; it shall be collected

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