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Note

Determination of benzo[a]pyrene in coke tars

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Polycyclic aromatic hydrocarbons (PAHs) are toxic substances found in increasing concentrations in the environment. Benzo[a]pyrene is carcinogenic and particularly hazardous, and methods for its determination in environmental and industrial samples have been investigated[1–5].

The aim of this work was to establish a method for the determination of benzo[a]pyrene in the tars originating from the coke plants. The method was intended to consist in the collection, extraction and isolation of benzo[a]pyrene from the coke tar, and its qualitative and quantitative determination by means of high-performance liquid chromatography (HPLC). For each stage we attempted to propose simpler approaches then those already established[6–8].

EXPERIMENTAL

The tar samples investigated originated from different black coals that were processed in different coke plants, and for this reason the results given here should not necessarily be considered as representative of products that may eventually be produced on a commercial scale.

A tar sample was homogenized with a mechanical stirrer until a uniform consistency was obtained. The sample was then dissolved in benzene using an ultrasonic stirrer. The insoluble parts gave a stable emulsion in the benzene solution obtained. To remove the insoluble part, a portion of this solution was placed on top of a non-pressurized chromatographic column filled with silica (Kieselgel H, 0.08–0.20 mm; E. Merck) that had been conditioned at 120°C and eluted with benzene. The first 50 cm^3 of eluate were collected, of which 1 cm^3 was applied to ready-made preparative chromatographic glass plates covered with silica (Kieselgel 60; E. Merck) and conditioned at 120°C for 0.5 h. On the same plates benzo[a]pyrene was additionally spotted as a chromatographic standard.

The chromatograms were developed with benzene–cyclohexene (3:2, v/v). The developed and dried chromatograms were examined under UV light and the band corresponding to benzo[a]pyrene was marked. It was then removed from the plate and eluted with benzene. From the solution obtained benzene was evaporated under the vacuum and the dry residue was dissolved in 1 cm^3 of cyclohexane.

To determine the mass loss of benzo[a]pyrene during the collection, extraction and isolation procedures we had to repeat all the above-described steps on a carefully

prepared "dummy" sample. Therefore, we added an appropriate and accurately weighed aliquot of benzo[a]pyrene to a known amount of silicone grease and homogenized this "dummy" sample using an ultrasonic stirrer.

The cyclohexane solution obtained was further analysed by HPLC using a chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia) consisting of an HPP 5001 pump, an LCD 2563 UV–VIS detector with a 290-nm filter, a TZ-4620 recorder, and a CI-100 integrator. Separation was achieved on a 150 × 3.6 mm I.D. column packed with 5-μm Separon SGX-C$_{18}$ (octadecylsilica) (Laboratorní Přístroje). The mobile phase was methanol–water (85:15, v/v) at a constant flow-rate of 0.7
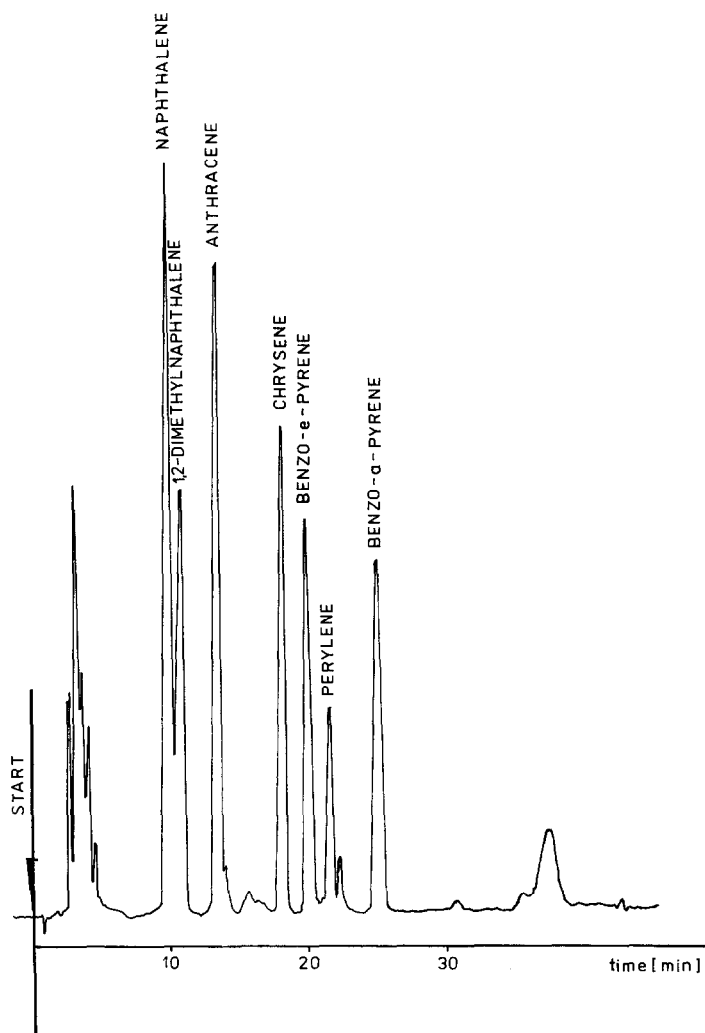

Fig. 1. Separation of a standard PAH mixture on a Separon SGX-C$_{18}$ column (150 mm × 3.3 mm I.D.). Mobile phase, methanol–water (85:15, v/v); flow-rate, 0.7 cm^3/min; pressure, 80 atm; detection, UV–VIS at 289 nm.
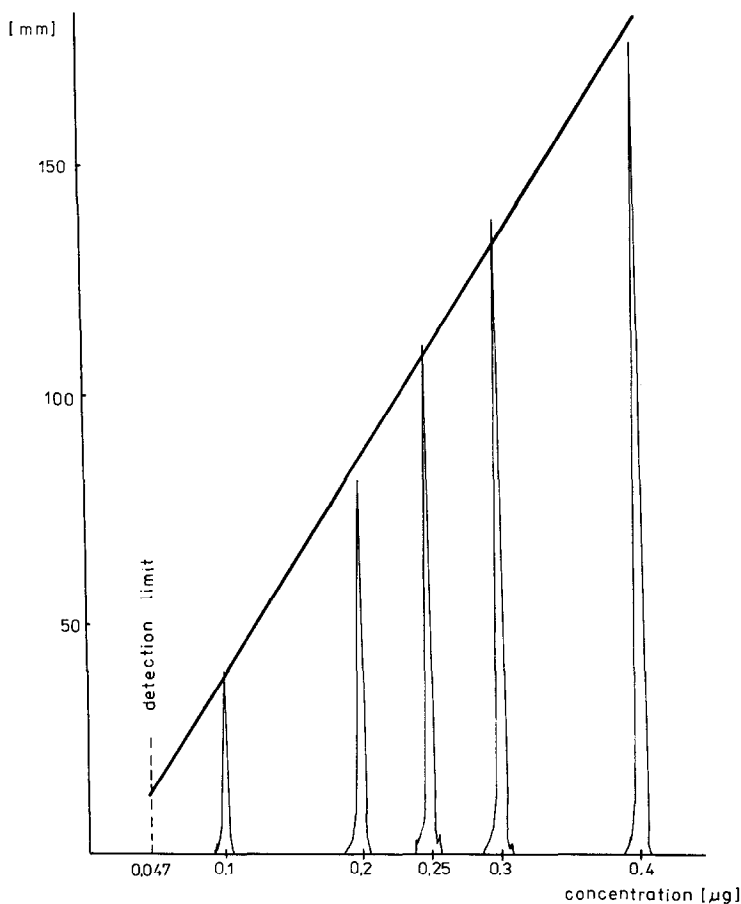
Fig. 2. Peak height vs. concentration of benzo[a]pyrene.

cm³/min. These conditions provided a good separation of benzo[a]pyrene from benzo[e]pyrene and other PAHs (see Fig. 1). Quantification was based on a previously constructed calibration graph (Fig. 2).

TABLE I

DETERMINATION OF THE BENZO[a]PYRENE (BaP) LOSS DURING SAMPLE PURIFICATION AND DETERMINATION OF THE CORRECTION FACTOR k

k was determined from the equation: actual amount of BaP $= k \cdot$ (determined amount of BaP).

Initial amount of BaP (mg/g of sample)	Determined amount of BaP (mg/g of sample)	Mean determined amount of BaP (mg/g of sample)	k
10	8.08		
10	8.15	8.11	1.233
10	8.10		

TABLE II

AMOUNT OF BENZO[a]PYRENE (BaP) IN THE COKE TARS FROM DIFFERENT SOURCES

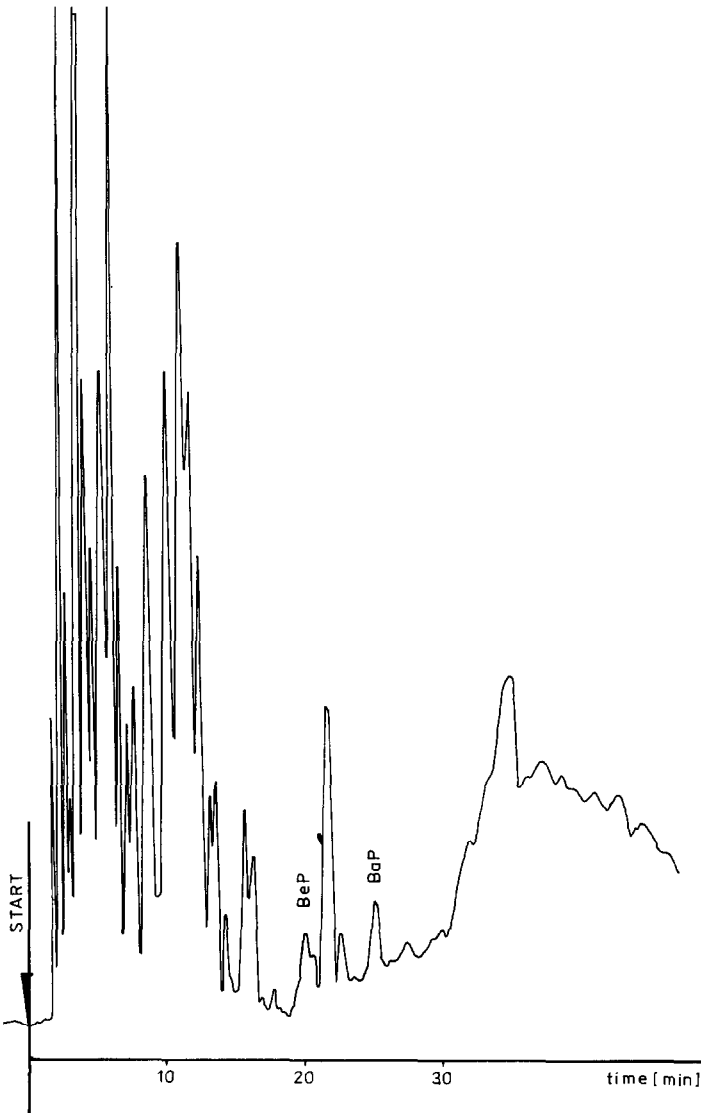| Sample No.	Amount of BaP determined (mg/g of sample)	Mean
1	1.27, 1.32, 1.30	1.30
2	2.73, 2.82, 2.75	2.77
3	3.18, 3.15, 3.20	3.18
4	3.88, 3.89, 3.85	3.87

Fig. 3. Separation of a PAH mixture originating from the coke tar. Conditions as in Fig. 1. BaP = benzo[a]pyrene; BeP = benzo[e]pyrene.

RESULTS

On the basis of the results obtained for the reference benzo[*a*]pyrene samples, carried through the routine purification procedure, we calculated the losses of this compound during the analytical procedure. The results are given in Table I.

Examples of the determination of benzo[*a*]pyrene in coke tars originating from different plants are shown in Table II. A chromatogram of PAHs separated from coke tar is given in Fig. 3.

CONCLUSIONS

The proposed method permits the separation and determination of benzo[*a*]-pyrene in coke tars. The content of benzo[*a*]pyrene depends on the origin of the tar (see Table II). The method can be extended to the determination of other PAHs, provided that the necessary calibration graphs are prepared in advance.

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