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Note

Determination of polycyclic hydrocarbons by channel thin-layer chromatography

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A variety of analytical procedures have been suggested for the determination of polycyclic hydrocarbons (PAH) in view of their toxicity and interest in their analysis in a variety of products. Although spectrophotometric and gas chromatographic procedures are usually applied in order to isolate and determine the various hydrocarbons, there is a need for a rapid and reliable method that will give the total PAH content. Only one procedure, involving extraction with a selective solvent (dimethyl sulphoxide) and UV adsorption, has been suggested for the determination of PAH in specific materials¹.

This paper describes a procedure based on the use of channel thin-layer chromatography (TLC) for this purpose. The term channel TLC²⁻⁴ is used to describe a procedure in which components that have to be fractionated on a thin plate are made to flow into narrow development channels in order to prevent the spreading of the chromatographic spot. In channel TLC, the chromatographic spot has a rectangular shape and both its area and length are related to the concentration of the eluted species.

Channel TLC can be applied to PAH analysis, as these compounds have similar R_F values in controlled chromatographic operating conditions and are fluorescent under UV light, so that their quantitative determination can be achieved in a simple manner.

EXPERIMENTAL

Channel TLC is carried out by scoring channels in a ready-to-use silica gel plate with a metal stylus and a template, and drawing two bent lines at the end of the channel, where a sample of the mixture to be analyzed is placed¹. Two sets of Merck (Darmstadt, G.F.R.) silica gel plates (20 × 5 cm with a thickness of 0.25 mm) were used, one set containing a fluorescence indicator.

All PAH were obtained commercially from Fluka (Buchs, Switzerland), BDH (Poole, Great Britain), Aldrich (Milwaukee, Wisc., U.S.A.) and Schuchardt (Munich, G.F.R.).

All chromatograms were run with the use of *n*-hexane-benzene (1:1) as the

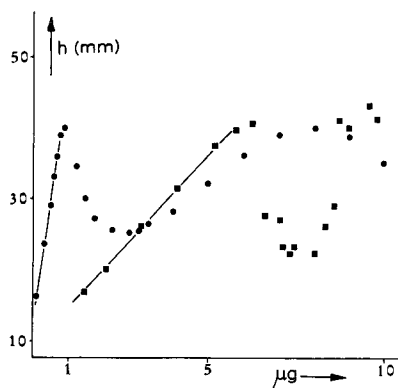


Fig. 1. Length of spots *versus* amount of 3,4-benzofluoranthene. ●, Silica gel plate; ■, silica gel plate containing a fluorescence indicator.

elution solvent. TLC was carried out with the chromatographic chamber in a water thermostat.

A large number of experiments were carried out in order to determine various factors that affect the quantitative determination of PAH by channel TLC, as indicated below.

In Fig. 1, the length of the chromatographic spots obtained on the two types of silica gel plates is plotted *versus* the amount of 3,4-benzofluoranthene applied. This five-ring hydrocarbon was selected as it is normally present in any PAH mixture in a fairly high concentration and has physico-chemical properties that are similar to the average values for most PAH. The two plots were similar. In both instances there is a linear relationship in the low concentration range, which for a silica plate containing a fluorescent indicator is in the range 1–6 μg , and for the other plate 0.1–1.0 μg .

This relationship was checked further in the experiments summarized in Fig. 2,

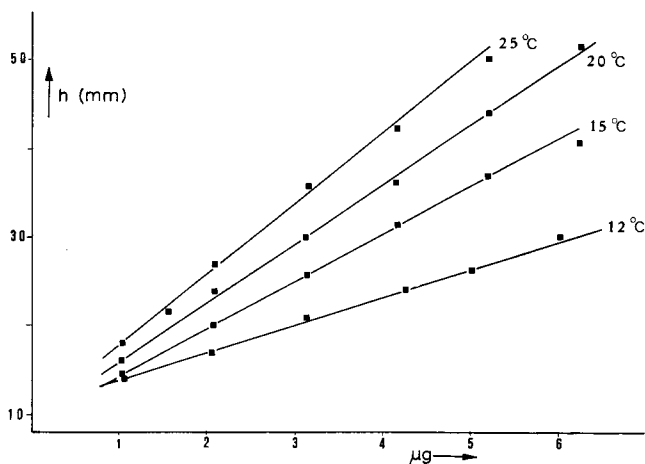


Fig. 2. Length of spots *versus* amount of 3,4-benzofluoranthene at different temperatures of the chromatographic chamber.

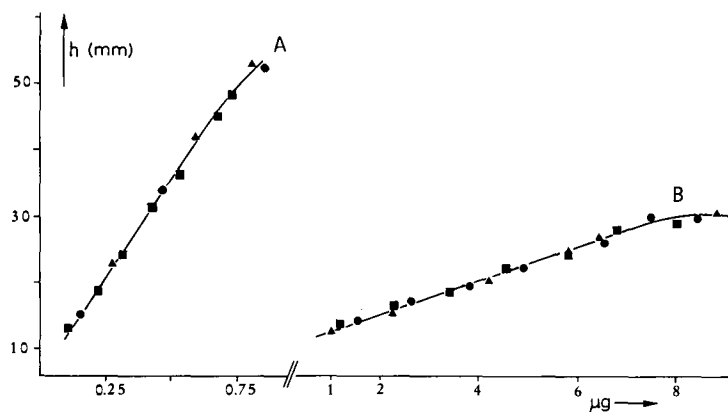


Fig. 3. Length of spots *versus* amount of different PAH standard mixtures. ▲, Mixture (a), containing 1,2-benzopyrene, chrysene, pyrene, 3-methylpyrene and phenanthrene; ■, mixture (b), containing 3,4-benzofluoranthene, indeno(1,2;3-*ed*)pyrene, 9-methylphenanthrene, coronene, 3-methylcholanthrene, perylene and fluoranthene; ●, mixture containing the components of (a) and (b). A, Silica gel plates; B, silica gel plates containing a fluorescence indicator.

different amounts of 3,4-benzofluoranthene being chromatographed by channel TLC in the temperature range 12–25°. The plots show that the development of the chromatograms is sensitive to temperature changes and, in order to obtain reproducible results, it is necessary to operate at constant temperature. The range 15–18° is the most suitable for preventing shaded spots from being obtained and to obtain a fairly short development time (about 40 min).

Plots of chromatographic spot lengths *versus* concentration for various PAH, such as phenanthrene, indeno[1,2,3-*ed*]pyrene, benzo[*a*]pyrene and fluoranthene, are linear but they do not coincide as the molecular weight apparently influences the spot size. As in practice PAH are usually found in mixtures that contain a variety of these compounds, a large number of channel thin-layer chromatograms were obtained by using PAH mixtures that contained the most common hydrocarbons in various proportions. The results for three different PAH mixtures are summarized in Fig. 3, which shows that on both types of plate a linear relationship is obtained between spot length and PAH concentration. It is therefore possible to use channel TLC to determine PAH quantitatively in any mixture. By running an analysis of artificial mixtures of various composition, it has been found that the standard deviation is ± 0.02 when silica gel plates are used and ± 0.17 when chromatograms are run on plates containing a fluorescence indicator.

The average R_f with the selected solvent (*n*-hexane–benzene, 1:1) is about 0.6.

APPLICATIONS

The aim of the procedure is to analyze products rapidly in order to determine their PAH contents. The following procedure was used. The sample was extracted with benzene in either a Soxhlet apparatus or a separating funnel. Some preliminary chromatograms have to be obtained in order to establish the required dilution, as the volume of the benzene extract to be applied on the plate is 10–50 μ l and a linear

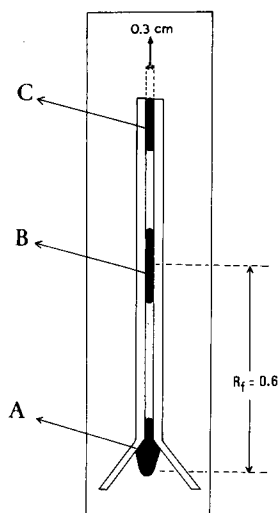


Fig. 4. Channel thin-layer chromatogram of a mixture containing (A) hydrophilic compounds, (B) PAH and (C) alkanes at 15°. Elution solvent: *n*-hexane–benzene (1:1).

relationship for PAH determinations is in the range 0.1–6 μg , depending on the silica gel plates used. The PAH concentration in the benzene solution must therefore be in the range 0.002–0.6 mg/ml.

The following materials were analyzed: atmospheric dust (100–500-mg sample), exhaust gases from a gasoline engine (collected in benzene) and lubricating oils (1 g dissolved in 100 ml of benzene).

A typical thin-layer chromatogram of a mixture containing hydrophilic compounds, PAH and alkanes is shown in Fig. 4.

The results obtained by channel TLC are usually 2–3 times higher than those obtained by conventional gas chromatography in which the total PAH content is determined by measuring the total surface area of the chromatographic peaks. As the accuracy of the procedure is good, it seems that most figures given previously for total PAH content are low because of the loss of volatile compounds and the fact that heavier compounds are not detected by conventional techniques.

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