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Note

Improved chromatographic evaluation of alkanes in atmospheric dust samples

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High-boiling *n*-alkanes occur extensively adsorbed on air-borne particulate matter. Their presence may be attributed to various sources, such as heating plants, the burning of oil or coal and car exhaust fumes. These hydrocarbons, with either an even or uneven number of carbon atoms, seem to be common components of urban dust, as they have been found in all samples¹. The existence of a large variety of components (polycyclic hydrocarbons, heterocyclic and hydrophilic compounds, etc.) in association with alkanes in the organic dust fraction necessitates a preliminary analytical separation.

The most common system for isolating the aliphatic hydrocarbons is based on a Soxhlet extraction of the dust with cyclohexane and subsequent fractionation of the different classes of compounds by partition with solvents of different polarity². Finally, the cyclohexane phase that contains the alkanes is analyzed by gas chromatography (GC) in order to determine the individual constituents³.

In this procedure, although the GC evaluation itself is sensitive and rapid, many preliminary steps are necessary in the preparation of the sample before it can be injected into the gas chromatograph; moreover, separation by solvent extraction is never complete and, consequently, the quantitative analysis is only approximate.

In order to find a more accurate and selective method for separating and identifying alkanes, we have applied a preparative thin-layer chromatographic (TLC) step to the cyclohexane solution, followed by a GC evaluation.

EXPERIMENTAL AND RESULTS

The TLC separation was performed by the ascending method with silica gel G (E. Merck, Darmstadt, G.F.R.) plates, 500 μ m thick, using *n*-hexane as the developer.

All of the alkanes were found together, with R_F values in the range 0.60–0.70, while polycyclic hydrocarbons had low R_F values and other more polar compounds, such as oxygen or nitrogen heterocyclic compounds, were very strongly retained near the starting point (Fig. 1).

The alkanes were detected by spraying the plates with iodine vapour and fluorescent polynuclear compounds were observed under a UV lamp.

The extraction efficiency was checked by running known amounts of alkanes on the plates; a recovery of about 95% was found.

The GC analysis was carried out on a Carlo Erba Fractovap Model GI chromatograph equipped with a flame ionization detector and a linear temperature programmer. The column used was a glass capillary, 80 m long and 0.28 mm I.D., with an efficiency of 80,000 theoretical plates. The silicone rubber SE-52, which is slightly polar and has good thermal stability, was used as the stationary phase.

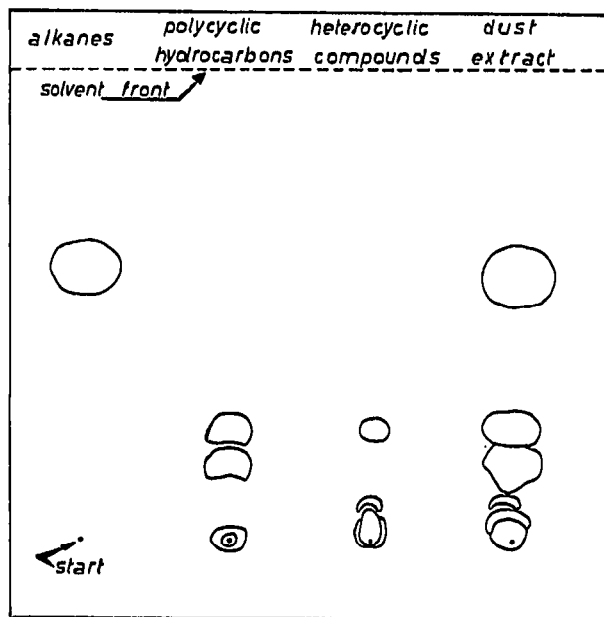


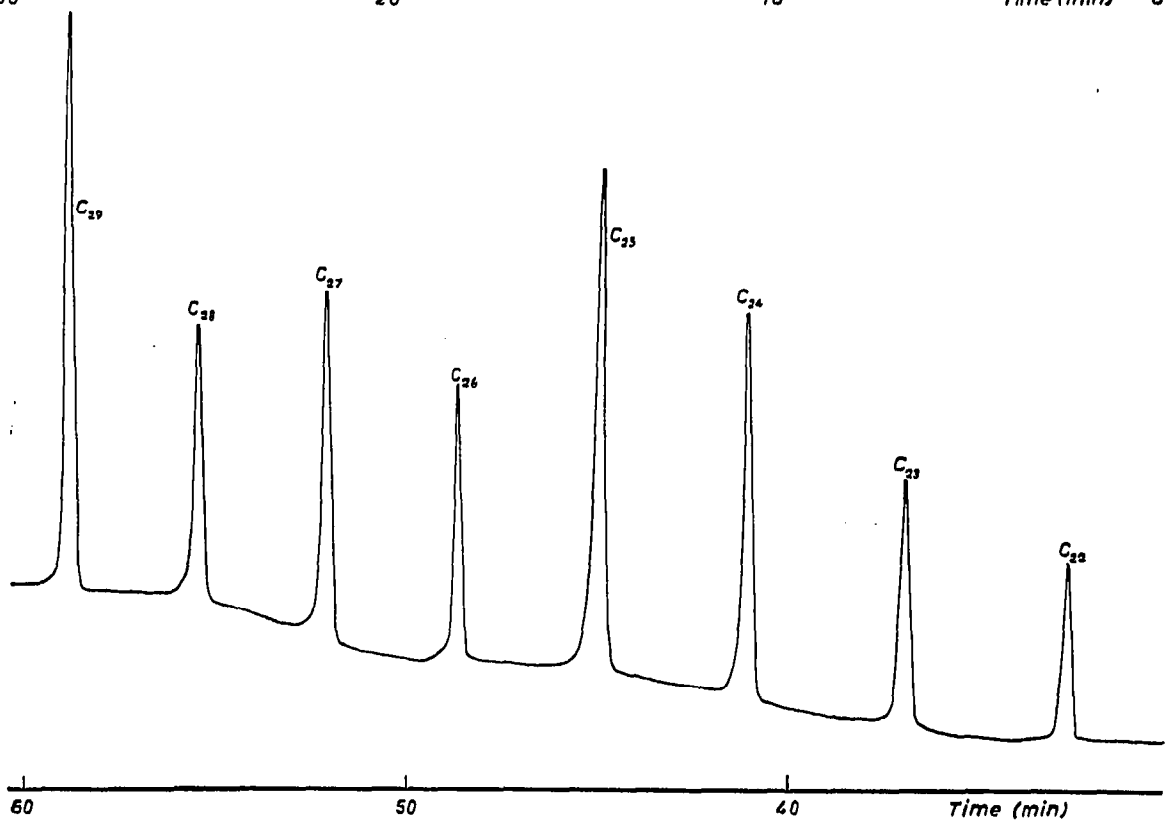
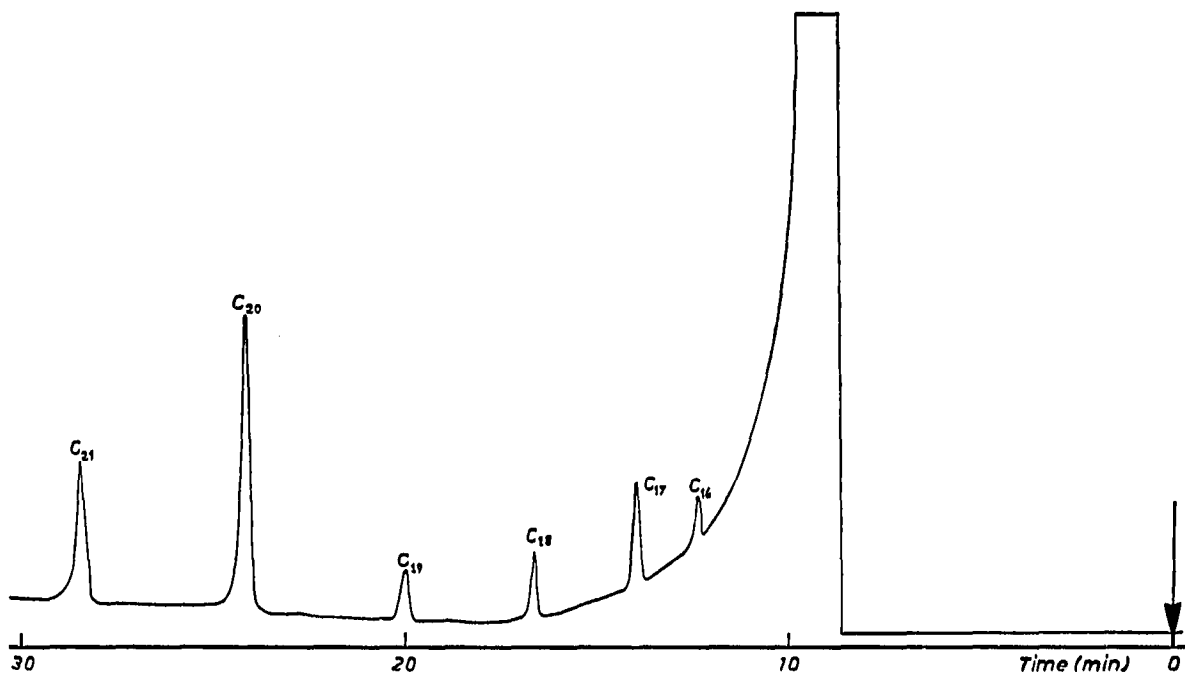
Fig. 1. TLC separation of *n*-alkanes from polycyclic hydrocarbons and heterocyclic compounds. Silica gel G plate, 500 μm thick; solvent, *n*-hexane.

PROCEDURE

Particulate matter is collected from the air by means of a high-volume air pump (Bendix 550) on a glass-fibre filter for the time necessary for about 50–100 mg of dust to be obtained.

The filter with the dust is extracted in a Soxhlet apparatus with 100 ml of cyclohexane for about 6–8 h. The solution is concentrated to 0.1 ml and transferred to a preparative thin-layer plate. A standard mixture of alkanes is placed on one side of the plate, which is developed with *n*-hexane. After drying, the part of the plate that contains the alkanes is separated and scraped from the plate into a sintered filter tube.

The compounds are then extracted two or three times with small portions of *n*-pentane. The pentane fractions are collected in a test-tube with a conical end and the solvent is evaporated so as to leave a volume of a few microlitres. For quantitative analysis, an internal standard (1,3,5-triphenylbenzene) is added. The pentane solution is analyzed by GC with temperature programming using the above



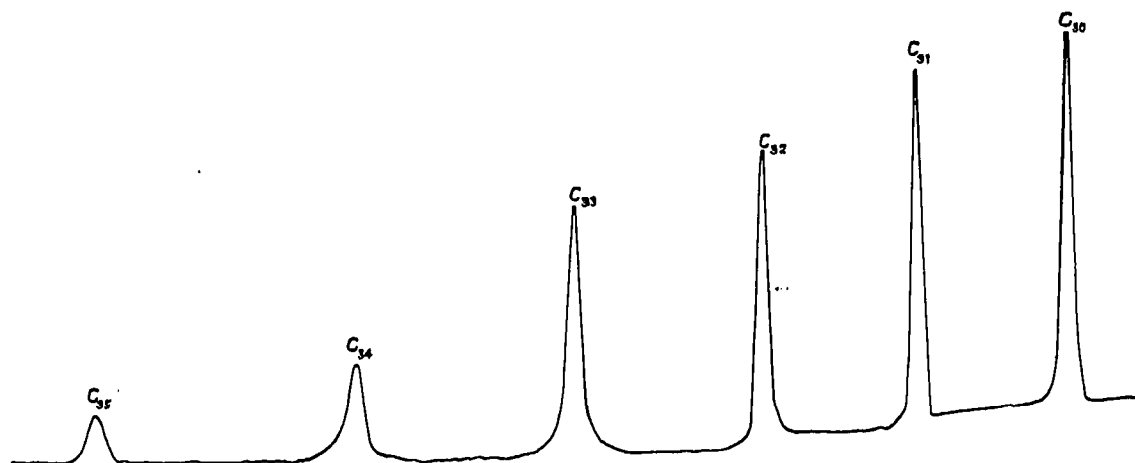


Fig. 2. Temperature-programmed gas chromatogram of a sample of an atmospheric dust extract (150–260° at 2.5°/min). Glass capillary column coated with SE-52.

column and the compounds are identified by comparing their retention times with those of standard alkanes measured under the same experimental conditions. The chromatogram of an atmospheric dust extract containing alkanes is shown in Fig. 2.

The results of the quantitative determination are given in Table I; all members of the linear series from C₁₆ to C₃₅ were present.

TABLE I
ALKANES IN ATMOSPHERIC DUST

<i>n</i> -Alkane	Amount in dust ($\mu\text{g/g}$)	<i>n</i> -Alkane	Amount in dust ($\mu\text{g/g}$)
C ₁₆	6.4	C ₂₆	102.8
C ₁₇	18.4	C ₂₇	126.4
C ₁₈	10.0	C ₂₈	100.8
C ₁₉	8.8	C ₂₉	132.8
C ₂₀	53.2	C ₃₀	81.6
C ₂₁	21.2	C ₃₁	89.6
C ₂₂	31.6	C ₃₂	38.0
C ₂₃	53.2	C ₃₃	39.6
C ₂₄	69.6	C ₃₄	14.0
C ₂₅	123.2	C ₃₅	12.0

CONCLUSION

The proposed method, which combines two efficient analytical techniques, can be used for the routine analysis of aliphatic hydrocarbons adsorbed on air-borne particles.

Because of the very sharp thin-layer separation of different classes of compounds, the direct application on the plate of a small amount (50 mg) of the atmospheric dust on a thin line at the starting point would also be possible.

REFERENCES

- 1 A. Liberti, *Pure Appl. Chem.*, 24(1970) 631.
- 2 M. B. Jacobs, *The Chemical Analysis of Air Pollutants*, Interscience, New York, 1960.
- 3 A. Liberti, G. P. Cartoni and V. Cantuti, *J. Chromatogr.*, 15 (1964) 141.