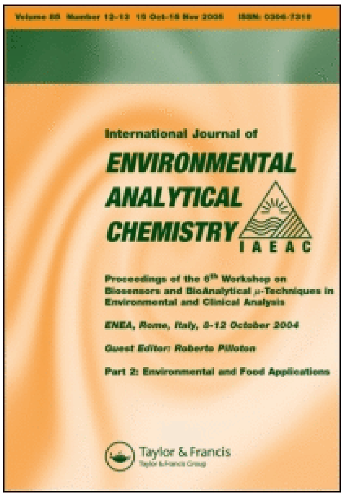

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High-Resolution GLC Profiles of Urban Air Pollutant Polynuclear Aromatic Hydrocarbons

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High-Resolution GLC Profiles of Urban Air Pollutant Polynuclear Aromatic Hydrocarbons

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KEY WORDS Air pollution, PAH, GLC, hydrocarbons.

A simple procedure was developed for the rapid separation and determination of the polynuclear aromatic hydrocarbons in urban air. By using sensitive detection and high-resolution glass capillary columns, profiles of polynuclears which are unique to the area of sampling were obtained. The potential of this method for effective screening of possible sources of atmospheric pollution is discussed.

INTRODUCTION

The analysis of the organic constituents of air pollution is dominated by concern with polynuclear aromatic hydrocarbons (PAH), because of the carcinogenic properties of many of these compounds. In addition, the presence of other air-borne chemicals may enhance the carcinogenic activity of these polycyclic hydrocarbons. The steadily increasing rate of lung cancer in industrial and polluted areas provokes deep concern over the control of air pollution and the identification of its possible sources.

The development of rapid screening methods without tedious pre-separation and clean-up procedures is necessary to establish simple standardized analytical procedures for identification of the hydrocarbons in urban atmospheres and determination of the pollution sources, i.e. factory, refinery, auto or aircraft, etc.

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Sawicki[1] reviewed the most important methods for determination of PAH and indicated that a lack of separation efficiency was the main obstacle to a better understanding of the composition. McPherson *et al.*[2] further demonstrated difficulties with achieving a sufficient degree of resolution using packed-column gas chromatography for direct determination of *n*-alkanes in the aliphatic fraction of airborne particulates. The present study was primarily undertaken to develop a profile method similar to the oil-spill identification by Adlard *et al.*[3] which would provide useful "fingerprint" chromatograms typical of particular sources of air pollution based on the use of high-resolution glass capillary column gas chromatography. Similar studies have already been attempted through high-resolution mass spectrometry.[4]

A simple extraction procedure, using cyclohexane as the solvent,[5] and then washing with nitromethane to remove the PAH,[6] involved the minimum number of steps to prepare the sample adequately for determination of air-pollution profiles by high-resolution GLC.

EXPERIMENTAL

Sample preparation

An 80 × 25 mm Soxhlet thimble was extracted with 100 ml of cyclohexane for 1 hour and the cyclohexane rejected. One half each of a series of 8 × 10 inch glass fiber filters, through which Indianapolis and Gary city air had been drawn for 24 hours (approximately 2000 m^3), was folded, placed in the thimble, and extracted for 3 hours with 100 ml of cyclohexane. The pale yellow solution was evaporated under reduced pressure to a volume of 20 ml on a 50°C water bath, and 10 ml of this solution was extracted 5 times with 5 ml of pre-equilibrated nitromethane. The remaining 10 ml of solution, the 10 ml of extracted cyclohexane, and the nitromethane extract were evaporated to dryness as described above. A "clean" filter was extracted in the same manner and used as a blank.

Gas chromatography

Approximately 20 μl of cyclohexane were added to the residue from each of the total-extract cyclohexane and washed cyclohexane fractions. A 0.1 μl aliquot of the resulting solution was injected onto a 50 meter × 0.23 mm, i.d., glass capillary column coated with an SE–52 methylphenylsilicone elastomer. The temperature was programmed from 50°C at 2°C/min. A Perkin–Elmer 990 gas chromatograph equipped with a flame ionization detector was used through these experiments.

150 μl of methylene chloride were added to the residue from each of the evaporated nitromethane fractions. 3 μl of this solution were then transferred to a precolumn[7] consisting of 2 mg of a specially treated solid support packed into a 1 mm i.d. glass tube. The solvent was then flushed off at room temperature with helium, and the glass tube was placed in the modified injection port of a Varian 1400 gas chromatograph. With the injection port at 250°C and the analytical column at room temperature, carrier gas was passed through the tube for 30 min to thermally release and trap the PAH onto the first part of the column. Temperature was then programmed from 120° to 250°C at 1.5°C/min.

RESULTS AND DISCUSSION

Chromatography of crude filter extracts was first attempted, but the chromatograms obtained were dominated so profoundly by *n*-alkanes that other trace organics could not be adequately detected. Therefore, a need for selective partitioning of *n*-alkanes and PAH was obvious. Figure 1 (A and B) shows chromatograms of the cyclohexane fractions after selective removal of PAH. These two samples were obtained from filters from two different locations in Gary, Indiana. Although the two chromatograms exhibit minor quantitative differences, the same range of *n*-alkanes is typically retained. Similar results were also obtained from other locations.

On the other hand, the chromatographic profiles of PAH extracted into nitromethane show qualitative and quantitative differences (Figures 2 and 4) which seem to be characteristic of each respective sampling area. For instance, representative chromatograms from four different locations in Indianapolis (Figures 2 (A–C), 4(A), and Table 1) are likely to reflect different sources of air pollution.

It is further shown that a high degree of resolution of the PAH obtained from air-pollution samples can be achieved with efficient glass capillary columns. Just as with the PAH mixtures obtained from tobacco smoke condensate,[8] the presence of numerous isomers in the range studied (from dicyclic up to hexacyclic systems) is obvious. While the complete analysis of such samples will need more complicated analytical schemes, the potential of this simple method for screening purposes is strongly suggested. Some PAH were tentatively identified from the retention times of standards (Figure 3), but combined gas chromatography-mass spectrometry will definitely be needed for positive identification. In a recent study by Lao *et al.*[9], some PAH from airborne particulate samples were so identified. Although further chromatographic resolution would still be desirable, definite limitations are imposed due to the high temperatures used. However, the SE-52

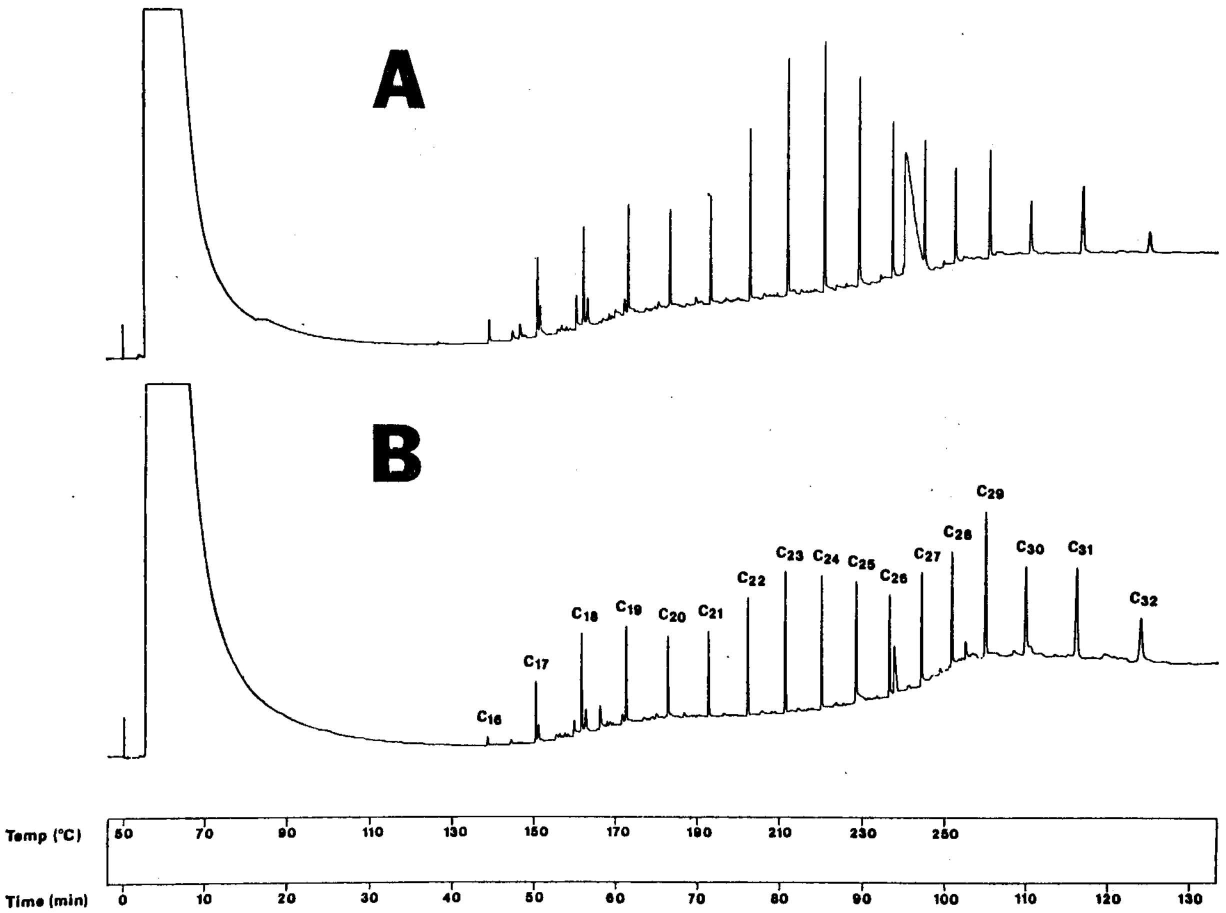

FIGURE 1 Chromatograms of cyclohexane fractions, after removal of polynuclear aromatic hydrocarbons, of air pollution samples from two locations in Gary, Indiana. Column: 50 m × 0.23 mm i.d. glass capillary coated with SE–52.

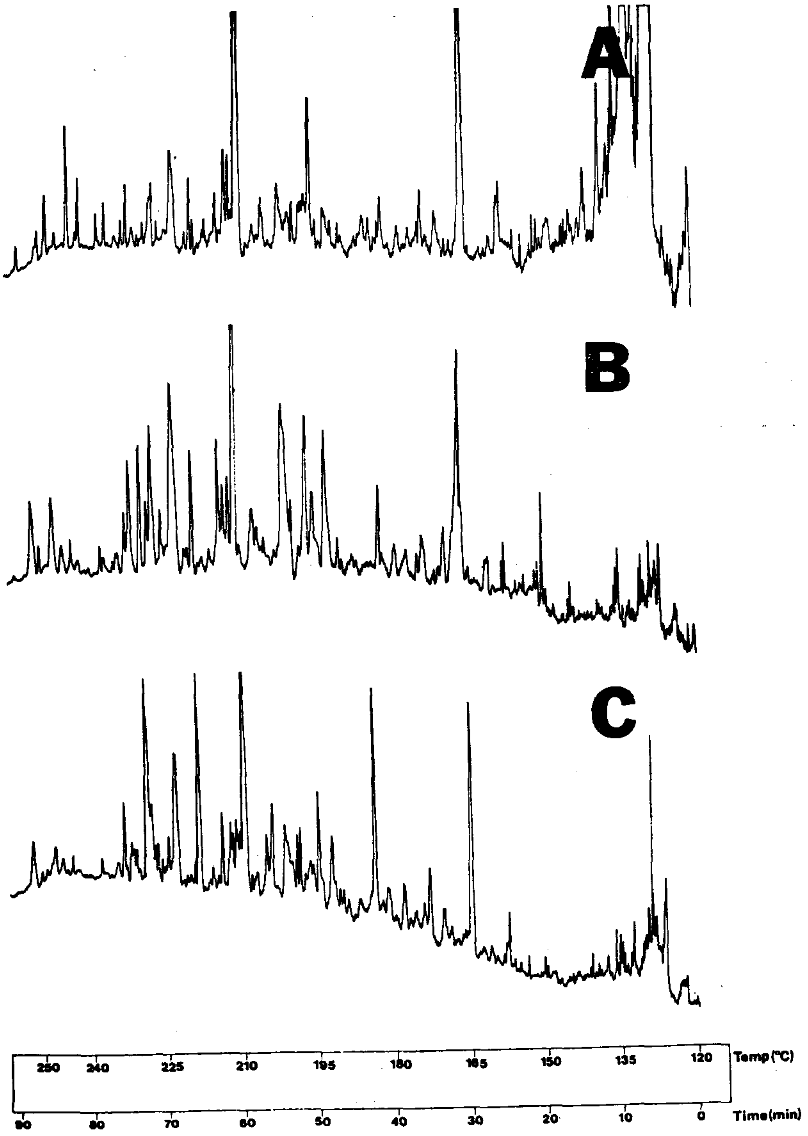

FIGURE 2 Chromatograms of nitromethane extracts of air pollution samples from three locations (see text and Table 1) in Indianapolis, Indiana. Column as in Figure 1.

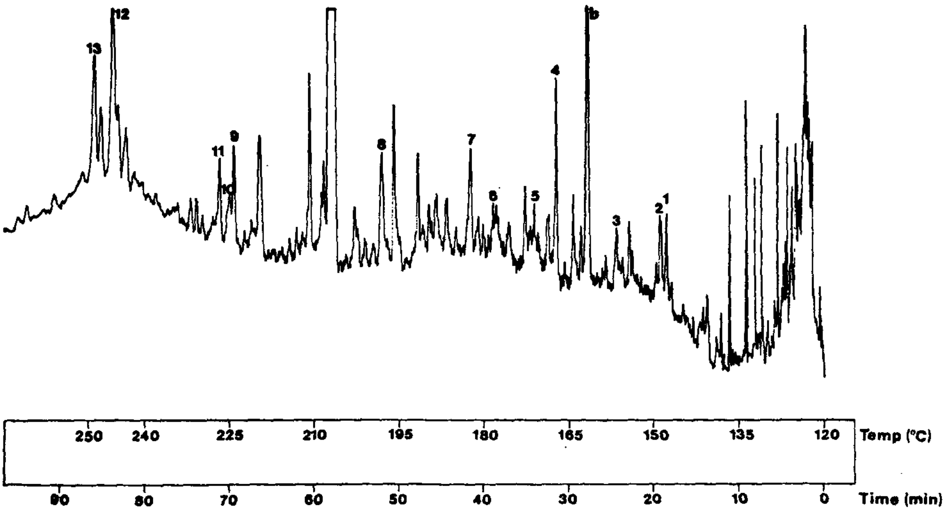

FIGURE 3 Chromatogram of nitromethane extract of an air pollution sample from Gary, Indiana. Column as in Figures 1 and 2. Key: 1, phenanthrene; 2, anthracene; 3, 4,5-methylene phenanthrene; 4, fluoranthene (added); 5, pyrene; 6, benz[*a*]fluorene; 7, 3-methylpyrene; 8, chrysene+triphenylene; 9, benz[*a*]pyrene; 10, benz[*e*]pyrene; 11, perylene; 12, dibenz[*a*, *c*]anthracene; 13, picene; b, peak found in extracts of blank filters (see Figure 4).

capillary column used here provided adequate resolution of benzo[e]-pyrene and benzo[a]pyrene.

The reproducibility of chromatograms has been significantly enhanced by using the precolumn technique. Larger amounts of accurately diluted solutions can now be easily transferred to the precolumn. Reproducibility of the extraction and partition steps used prior to high-resolution gas chromatography is adequate. Figure 4 (A and B) shows chromatograms of the nitromethane fractions obtained from an Indianapolis air-pollution filter which was cut in half and the two parts processed separately. Figure 4(C) corresponds to the blank obtained by analyzing a "clean" filter. This chromatogram shows the presence of only several minor peaks. The most prominant peak in the first portion of the chromatogram corresponds to a contaminant appearing in all other chromatograms. The large fluoranthene peak in Figure 3 has its origin in "spiking" the filter for quantitative purposes.

Once the constituents of air-pollutant profiles are identified, this method may be useful in yielding rapid information about the presence or absence of

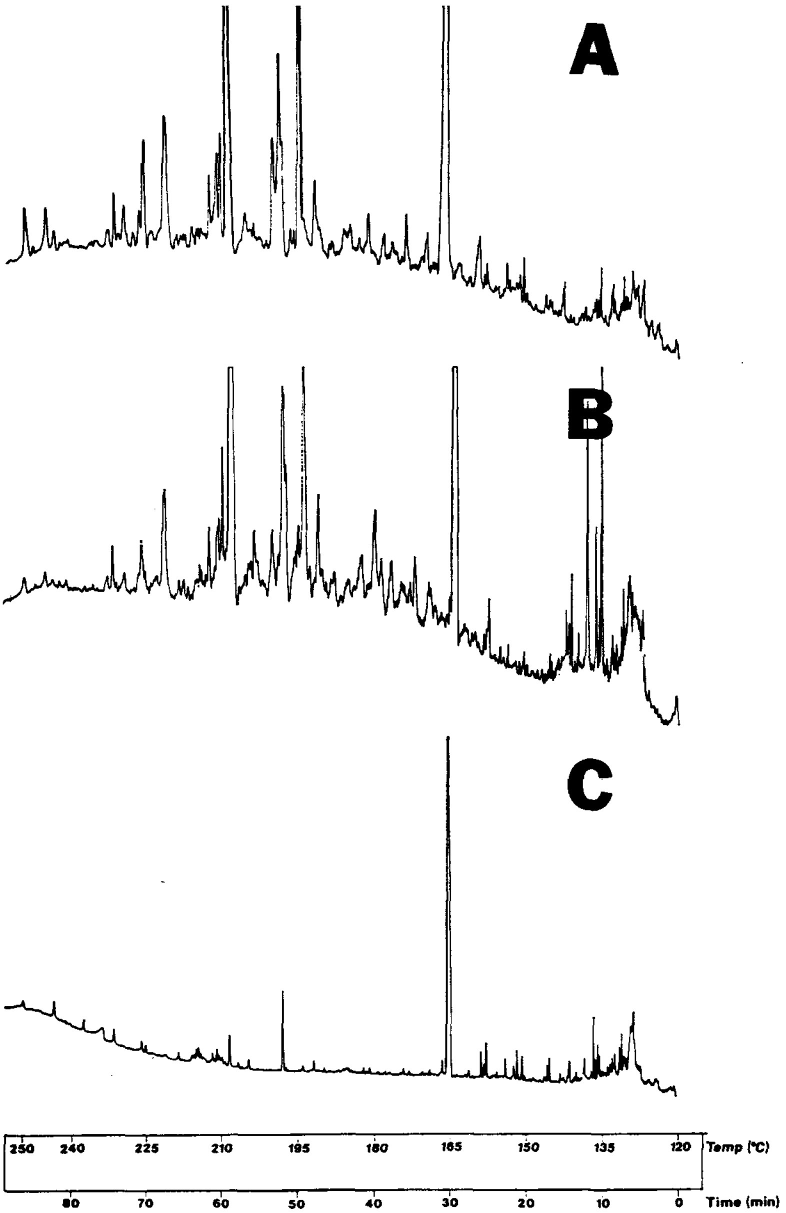

FIGURE 4 Chromatograms of nitromethane extracts of (A and B) two halves of one air pollution sample from Indianapolis, Indiana, and (C) a "clean" filter. Column as in Figures 1, 2, and 3.

TABLE I

Chromatogram No.	Location	Possible pollution sources	Fuel
2 (A)	industrial	power plant	coal
		automobile factories	coal
		chemical plants	
		airport	jet fuel
		homes	oil and gas
2 (C)	inter-city residential	plating plant	oil
		homes	oil and gas
2 (B)	downtown	auto exhaust	gasoline and diesel fuel
4 (A and B)	suburban	homes occasional pollution from nearby oil refinery possible (depending on meteorological conditions)	oil and gas

certain potent carcinogens in a given sample. It should also be remembered that profiling for PAH may be just one of several alternatives for the identification of air-pollution sources. In a similar fashion, high-resolution capillary columns could be combined with selective detectors in order to establish the presence of other air-pollution components which are typical of a given location.

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