

# Lithium Chloride as a Gas Chromatographic Substrate for Polynuclear Aromatic Hydrocarbons

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In spite of recent advances in technique (5-7), the isolation and identification of higher molecular weight polynuclear aromatic hydrocarbons (PAH) in heated natural substances and pyrolytic products therefrom remains a formidable task. The core of the problem is the separation of a pure component from the multiplicity of compounds usually found, e.g. at least 81 PAH in cigarette-smoke condensate (2). The obvious advantages of gas-liquid chromatography have prompted many investigators to apply this technique to the problem, with some success. Because of the high boiling points of many of the PAH, relatively heat-stable organic substances have been employed as substrates, e.g. silicone grease, Apiezon, etc. (1, 6); however, all of these possess serious shortcomings. At temperatures necessary for elution of many of the PAH (>280°C in some cases), severe bleed-off of substrate may occur, resulting in short column life and a shifting baseline, especially when programming. Under isothermal conditions, improved

baseline stability is observed, but some resolution is lost and column life is still short. Although capillary columns utilizing newer heat-stable organic substrates (1) have overcome some of these difficulties, such columns are of no value when collection of eluted peaks is desired.

The present report concerns the use of lithium chloride as a gas chromatographic substrate for PAH, which eliminates the above shortcomings, shows improved resolution for some components, and permits injection of sufficient quantities to allow peak collection. Although inorganic salts (including lithium chloride) and eutectic mixtures have been previously used as gas chromatographic substrates (3, 4) the special capabilities of such substances for the separation of higher molecular weight PAH have not been fully appreciated.

Figure 1A illustrates the chromatogram obtained with a mixture of aromatic hydrocarbons (5  $\mu$ g. each) having from two to seven rings and boiling from 182°C. (indene) to about 600°C. (coronene)

(6). The substrate was 20% lithium chloride on Chromosorb P ( $\frac{1}{8}$  inch x 8 feet stainless steel column); the temperature was programmed from 80°C. to 320°C. at 2°C. per minute and flame ionization detection was employed. No baseline shift is observed throughout the programming. Benzo[a]pyrene elutes after benzo[e]pyrene but the two peaks are not resolved in mixtures, except for a slight inflection. A generally similar elution pattern is observed on chromatography of larger amounts (300  $\mu$ g. each) of PAH on a  $\frac{1}{4}$  inch x 8 feet column of the substrate programmed from 120°C. to 360°C. at 4°C. per minute using thermal conductivity detection. The retention temperatures are higher, but improved resolution is observed for the benzopyrene isomers (Figure 1B). Except for a recent report using capillary columns (1), we are aware of no previously published work showing even partial separation of these isomers; in fact, the capillary column separation of the benzopyrenes is no better than that illustrated in Figure 1B. With the

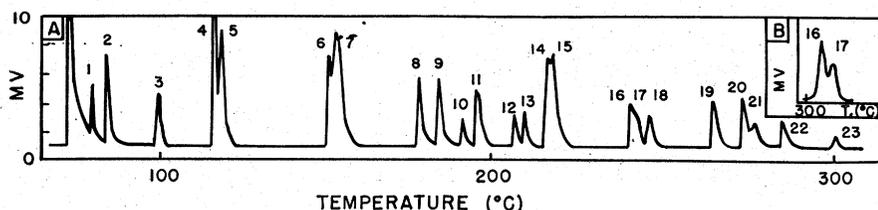


Figure 1. Separation of polynuclear aromatic hydrocarbons on lithium chloride columns.

A. Entire chromatogram,  $\frac{1}{8}$  inch x 8 feet column programmed from 80°C. at 2°C. per minute.

B. Partial chromatogram showing some resolution of benzopyrene isomers ( $\frac{1}{4}$  inch x 8 feet column programmed from 120°C. at 4°C. per minute).

(1) naphthalene, (2) indene, (3) 2-methylnaphthalene, (4) 2,6-dimethylnaphthalene, (5) acenaphthene, (6) 9-methylfluorene, (7) anthracene and phenanthrene, (8) fluoranthene, (9) pyrene, (10) 9,10-dimethylantracene, (11) 2-methylpyrene, (12) benzo[b]fluorene (13) 7-H-benzo[c]fluorene, (14) benzo[b]phenanthrene and triphenylene, (15) benz[a]anthracene, benz[b]anthracene, and chrysene, (16) benzo[e]pyrene, (17) benzo[a]pyrene, (18) benzo[b]fluoranthene, (19) 3-methylcholanthrene, (20) dibenz[a,c]anthracene and dibenz[a,j]anthracene, (21) dibenz[a,h]anthracene, (22) coronene, (23) dibenzo[a,i]pyrene.

particular conditions used here, perylene also elutes with benzo[a]pyrene. The retention temperatures are dependent upon the starting temperature and the rate of programming. When using a starting temperature of 100°C., the retention temperatures are about 30°C. higher when programming at 4°C. per minute compared to 1°C. per minute.

Using the larger diameter column and thermal conductivity detection, peaks may be collected in the usual manner for further work. In some cases, peaks containing one

or more components, e.g. benzo[a]pyrene and perylene, may be collected and the components differentiated by fluorescence analysis, e.g. determining benzo[a]pyrene in the presence of perylene by collection in concentrated sulfuric acid (8). In other cases, thin layer chromatographic separations of eluted peaks may be of value (6, 8).

The separation is not entirely on the basis of boiling point, indicating some affinity of the inorganic substrate for PAH. Since lithium chloride (m.p. 614°C.) is a solid under the chromatographic conditions, the

separation involves gas-solid chromatography instead of the gas-liquid systems in effect with the usual organic substrates. At present, we are successfully using this method in studies on the pyrolysis products of certain tobacco pigments. ■

*Mention of specific commercial product does not constitute endorsement of the product over others of a similar nature by the USDA.*

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